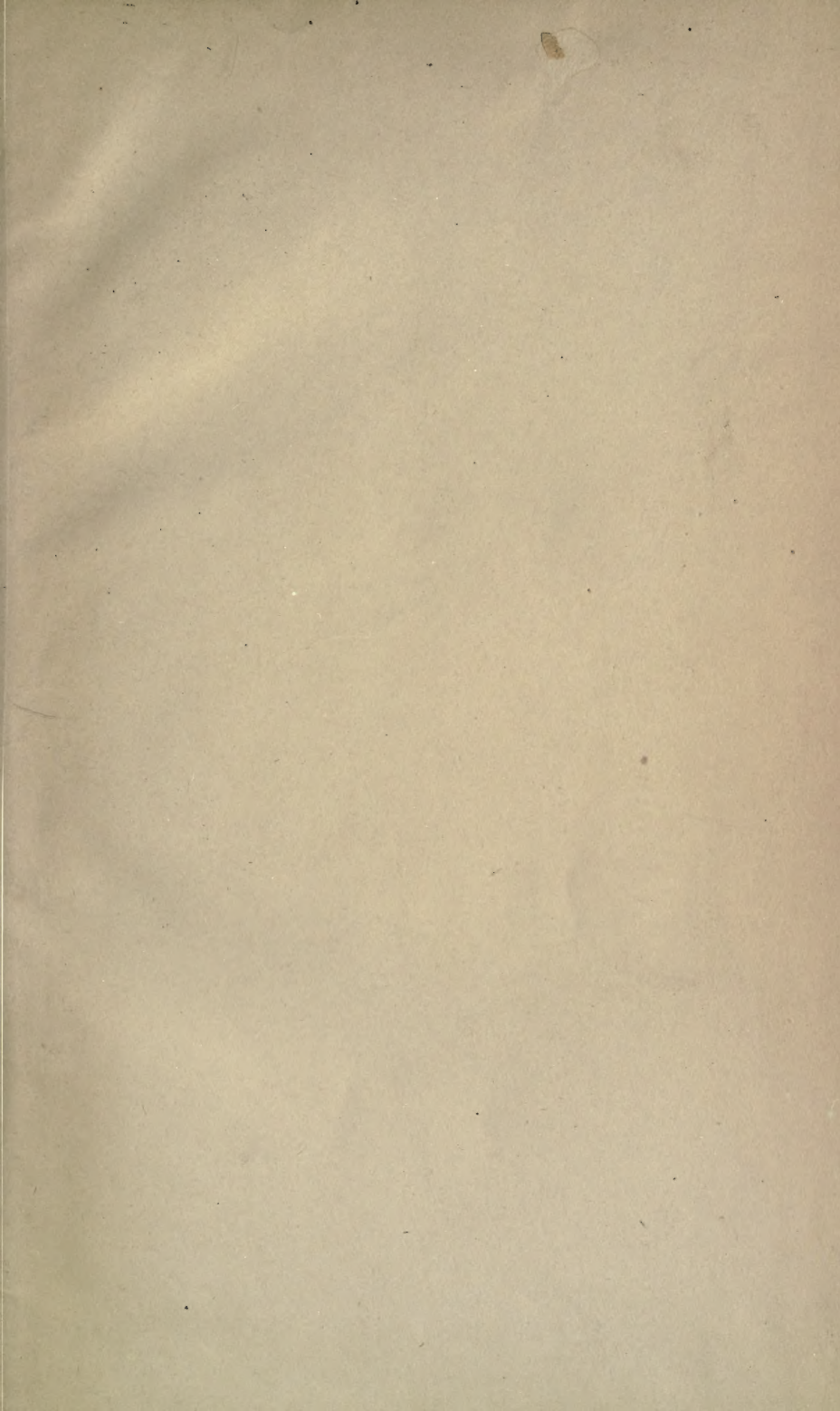



3 1761 05477346 0

Nov 20





Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

WORKS OF PROF. H. L. WELLS

PUBLISHED BY

JOHN WILEY & SONS.

Manual of Qualitative Chemical Analysis.

By the late Dr. C. REMIGIUS FRESENIUS, Privy Aulic Counsellor and Professor, Director of the Chemical Laboratory at Wiesbaden. Authorized translation by HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New edition, thoroughly revised, from the sixteenth German edition. 8vo, 764 pages, cloth, \$5.00.

A Laboratory Guide in Qualitative Chemical Analysis.

Designed for use in connection with Fresenius's Manual of Qualitative Chemical Analysis. 8vo, 200 pages, cloth, \$1.50.

C
W4554kx

A LABORATORY GUIDE

IN

QUALITATIVE CHEMICAL ANALYSIS.

BY
H. L. WELLS, M.A.,

*Professor of Analytical Chemistry and Metallurgy in the
Sheffield Scientific School of Yale University.*

FIRST EDITION.

FIRST THOUSAND.


90706
25/8/08.

NEW YORK:

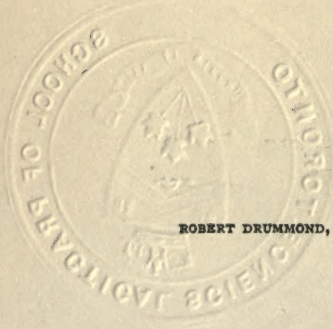
JOHN WILEY & SONS.

LONDON: CHAPMAN & HALL, LIMITED.

1901.



Copyright, 1898,
BY
H. L. WELLS.



ROBERT DRUMMOND, ELECTROTYPYER AND PRINTER, NEW YORK.

PREFACE.

THE method of instruction presented in this little book has been developed by the author in teaching the subject during the past fourteen years. The course differs materially from those usually employed, and has given satisfaction because of its tendency to obviate thoughtless and mechanical work on the part of the student—facts which may be offered as an excuse for adding another to the great number of works on qualitative analysis. The general plan of Part I, which is applied wherever it would not be too cumbersome, consists in giving directions for analyses without mentioning the results, and in requiring the student to determine for himself the results of the operations. Following this system, the student almost invariably performs his preliminary experiments with great care, because he recognizes their object and importance. This is especially the case if the student understands that, in the analysis of unknown mixtures, he will not be allowed to use any tables or abbreviated schemes of analysis.

The methods of analysis given by Fresenius are chiefly used, but a number of changes have been made where experience has shown them to be advantageous on account of simplicity or accuracy. A few novelties are introduced in the way of details of processes or combinations of methods, but it may be stated that these have been thoroughly tested and may be relied upon as trustworthy. An original method, now published for the first time, is used for the detection of chlorides in the presence of bromides. Lithium has been

included among the commoner metals, on account of the extensive use of its salts in medicine and their commercial abundance. This addition considerably increases the interest of the alkali-metal group.

The book is not intended to be a complete and independent work on analytical chemistry, and students who use it should be encouraged to increase their knowledge of the subject by frequent reference to a comprehensive text-book.

Before beginning the study of qualitative analysis, the student should possess a good knowledge of elementary chemistry, including the fundamental chemical theories; but there is much theoretical knowledge to be gained, or more firmly grasped, in connection with the study of analysis. On this account, a section of the book (Part II) is devoted to the explanation of the formation of formulas and equations, and to some other points of theory which have a special bearing upon the course of study, including the important subject of ionization.

Part III contains an alphabetical arrangement of the radicals, with brief descriptions of the properties upon which the analytical methods are based. Most of the facts given there should be familiar to the student after completing the course presented in Part I, so that it will be useful in reviewing the subject. This part may be of use, also, for reference in regard to reactions, the formulas of precipitates, etc., and as an index to the fuller descriptions in Fresenius's Manual.

The author is under obligation to Dr. B. B. Boltwood and Mr. H. W. Foote, Instructors in the Sheffield Laboratory, for many valuable suggestions, and to Miss L. P. Bush for assistance in proof-reading.

NEW HAVEN, CONN., *May*, 1898.

TABLE OF CONTENTS.

PART I. ANALYTICAL COURSE.

	PAGE
NOTICE TO THE STUDENT.....	I
CHAPTER I. THE POSITIVE RADICALS (Metals).....	3
II. GROUP A. (Fresenius's Group V, Division I.) Radicals whose Chlorides are Insoluble or nearly Insoluble in Acidified Solutions.....	5
III. GROUP B. (Fresenius's Group V, Division II.) Radicals (excepting Ag ⁺ and Hg ⁺) whose Sulphides are Precipitated in Acid Solutions, and are Insoluble in Yellow Ammonium Sulphide	8
IV. GROUP C. (Fresenius's Group VI.) Radicals whose Sulphides are Precipitated in Acid Solutions, and are Soluble in Yellow Ammonium Sulphide.....	14
V. GROUP D. (Fresenius's Group III and Iron.) Radicals not included in the Preceding Groups, whose Hydroxides are Precipitated in the Presence of Ammonium Chloride by Ammonium Hydroxide	17
VI. GROUP E. (Fresenius's Group IV, excepting Iron.) Radicals not belonging to the Preceding Groups, whose Sulphides are Precipitated in Alkaline Solutions by Ammonium Sulphide	24
VII. GROUP F. (Fresenius's Group II, excepting Magnesium.) Radicals not belonging to the Preceding Groups, whose Carbonates are Precipitated by Ammonium Carbonate in the Presence of Ammonium Chloride in Alkaline Solutions.....	27
VIII. GROUP G. (Fresenius's Group I and Magnesium.) Radicals not belonging to the Preceding Groups.....	31
IX. THE SEPARATION OF THE GROUPS OF METALS FROM EACH OTHER.....	34
X. THE INORGANIC NEGATIVE RADICALS (Acids.).....	40
XI. GROUP A. (Fresenius's Group II.) Acid Radicals whose Silver Salts form Precipitates in Acid Solutions.....	43

CHAPTER	PAGE
XII. GROUP B. (Fresenius's Groups I and III.) Acid Radicals whose Silver Salts do not form Precipitates in Dilute Acid Solutions.....	48
XIII. THE ANALYSIS OF SOLIDS.....	57
XIV. THE REAGENTS.....	61

PART II. THEORY.

XV. CHEMICAL RADICALS AND FORMULAS.....	71
XVI. IONIZATION AND IONS.....	75
XVII. PRECIPITATION ?.....	79
XVIII. CRYSTALLIZATION FROM MIXED SOLUTIONS.....	81
XIX. THE FORMATION OF VOLATILE COMPOUNDS.....	83
XX. THE CLASSIFICATION OF RADICALS AND SALTS.....	84
XXI. CHEMICAL EQUATIONS.....	87

PART III. DESCRIPTIVE PART.

XXII. ALUMINIUM.....	101
XXIII. AMMONIUM.....	103
XXIV. ANTIMONY.....	104
XXV. ARSENIC.....	106
XXVI. BARIUM.....	108
XXVII. BISMUTH.....	110
XXVIII. BORATES.....	111
XXIX. BROMIDES.....	112
XXX. CADMIUM.....	114
XXXI. CALCIUM.....	115
XXXII. CARBONATES.....	117
XXXIII. CHLORATES.....	119
XXXIV. CHLORIDES.....	120
XXXV. CHROMIUM AND CHROMATES.....	121
XXXVI. COBALT.....	123
XXXVII. CUPRIC SALTS.....	124
XXXVIII. CYANIDES.....	125
XXXIX. FERRIC SALTS.....	126
XL. FERROUS SALTS.....	127
XLI. FLUORIDES.....	128
XLII. IODIDES.....	129
XLIII. LEAD.....	130
XLIV. LITHIUM.....	131
XLV. MAGNESIUM.....	132
XLVI. MANGANESE.....	133
XLVII. MERCURIC SALTS.....	134
XLVIII. MERCUROUS SALTS.....	135

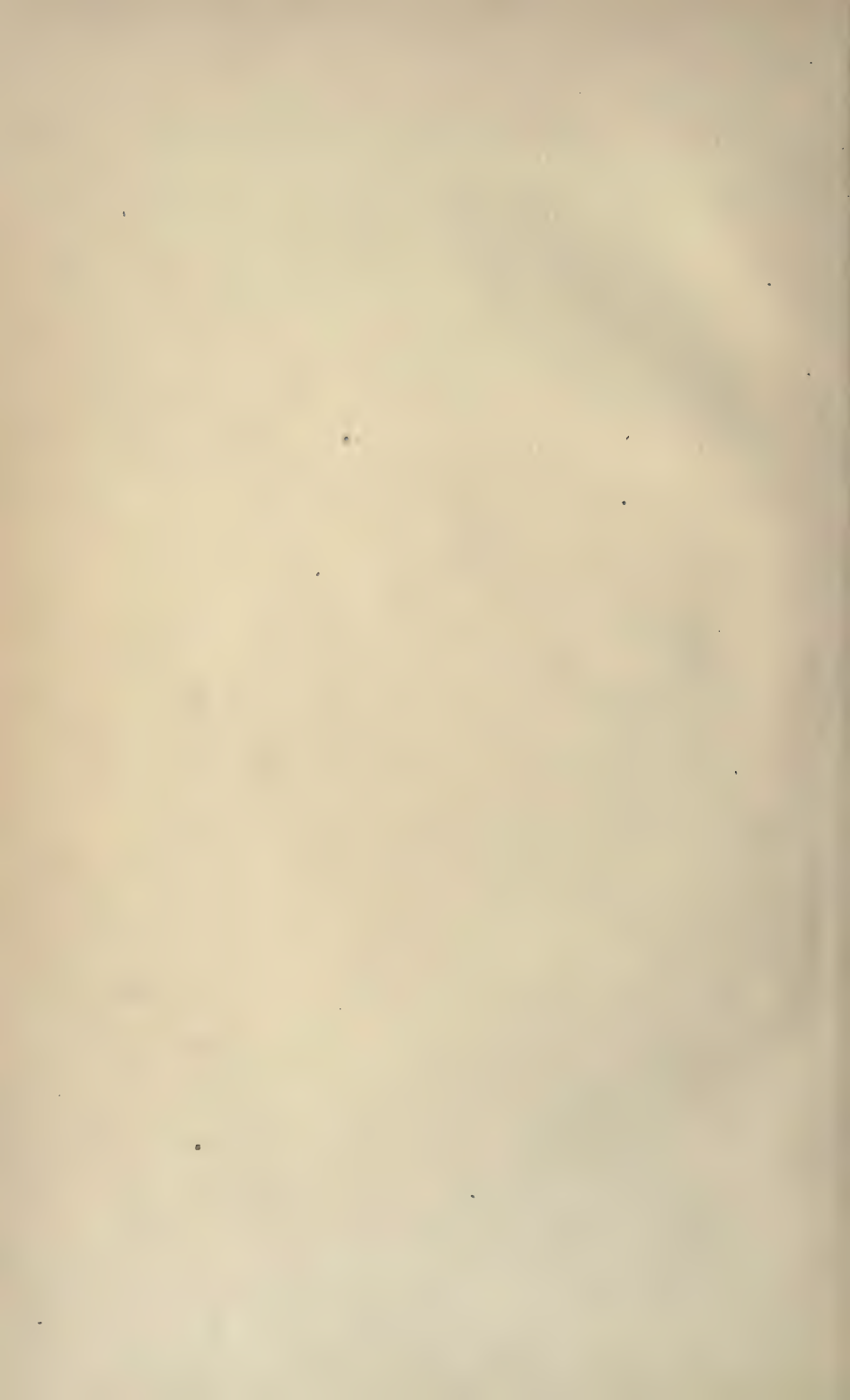
TABLE OF CONTENTS.

vii

CHAPTER	PAGE
XLIX. NICKEL.....	136
L. NITRATES.....	137
LI. OXALATES.....	138
LII. PHOSPHATES.....	139
LIII. POTASSIUM.....	141
LIV. SILICATES.....	142
LV. SILVER.....	143
LVI. SODIUM.....	144
LVII. STANNIC SALTS.....	145
LVIII. STANNOUS SALTS.....	146
LIX. STRONTIUM.....	147
LX. SULPHATES.....	149
LXI. SULPHIDES.....	150
LXII. ZINC.....	151

APPENDICES.

I. LIST OF APPARATUS.....	153
II. LABELS FOR EXPERIMENTAL SOLUTIONS.....	155
III. LABELS FOR REAGENTS.....	171



A LABORATORY GUIDE IN QUALITATIVE CHEMICAL ANALYSIS.

PART I. *ANALYTICAL COURSE.*

NOTICE TO THE STUDENT.

THE object of this course is to introduce the subject of qualitative analysis in such a way as to develop the powers of observation, inductive reasoning, and memory, and at the same time to give a knowledge of chemical facts and methods which will be of use in the further study of this and related subjects.

The student is earnestly requested to perform the indicated experiments in a thorough manner, and to consider carefully the chemical reactions taking place.

He should also learn the chemical facts from his own experiments, and afterwards confirm his observations by consulting Part III. Fuller information may be obtained from a book of reference. Fresenius's Manual of Qualitative Chemical Analysis is recommended for this purpose.

A note-book should be kept and the equations of all the reactions recorded in it. The note-book may be further used.

if expedient, to aid the memory, but should never be used in place of the memory. At the outset, it should be understood that the student is required to remember the facts encountered.

He is likewise strongly urged, while making analyses, not to have before him any analytical table or abbreviated scheme, either such as may be written out or those given in text-books. This will tend to prevent making analyses in a mechanical way, like cooking.

Other methods of analysis should not be substituted for those given in this course unless such a change is advised by the instructor.

Finally, it is essential to good work that everything should be kept neat and in order continually at the work-bench and elsewhere in the laboratory.

A list of the solutions used as reagents, showing how they are made, and mentioning their uses, is given in Chapter XIV. Wherever hydrochloric acid, HCl , nitric acid, HNO_3 , and sulphuric acid, H_2SO_4 , are mentioned without modification in this book, the ordinary, dilute solutions are meant.

CHAPTER I.

THE POSITIVE INORGANIC RADICALS (METALS).

FOR use in the experiments which follow, a set of solutions of salts of the commoner positive radicals considered in this course should be prepared. These may be made up by the instructor, but if time permits it is an advantage to the student to handle the salts and prepare his own solutions. The liquids should be filtered if not perfectly clear, placed in properly labeled bottles, and arranged, preferably in alphabetical order. The following table gives a list of the radicals taken into consideration, together with the formulas of the salts that may be conveniently used, and the number of parts by weight of water which may be taken to dissolve one part of the salt:

Al ⁺⁺⁺ , Aluminium,	$\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O} \dots\dots$	1 : 50
NH ₄ ⁺ , Ammonium,	$\text{NH}_4\text{Cl} \dots\dots\dots$	1 : 20
Sb ⁺⁺⁺ , Antimonious,	SbCl_3 with HCl $\dots\dots\dots$	1 : 50
As ⁺⁺⁺ , Arsenious,	AsCl_3 (As_2O_3 in HCl) $\dots\dots\dots$	1 : 50
Ba ⁺⁺ , Barium,	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \dots\dots\dots$	1 : 20
Bi ⁺⁺⁺ , Bismuth,	$\text{Bi}(\text{NO}_3)_3$ with $\text{HNO}_3 \dots\dots\dots$	1 : 50
Cd ⁺⁺ , Cadmium,	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \dots\dots\dots$	1 : 50
Ca ⁺⁺ , Calcium,	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \dots\dots\dots$	1 : 20
Cr ⁺⁺⁺ , Chromium,	$\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O} \dots\dots\dots$	1 : 50
Co ⁺⁺ , Cobalt,	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \dots\dots\dots$	1 : 50
Cu ⁺⁺ , Cupric,	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \dots\dots\dots$	1 : 50
Fe ⁺⁺⁺ , Ferric (Iron),	$\text{FeCl}_3 \cdot ?\text{H}_2\text{O} \dots\dots\dots$	1 : 50
Fe ⁺⁺ , Ferrous (Iron),	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \dots\dots\dots$	1 : 50

Pb ⁺⁺ ,	Lead,	Pb(NO ₃) ₂	1:20
Li ⁺ ,	Lithium,	LiCl.....	1:20
Mg ⁺⁺ ,	Magnesium,	MgCl ₂ .6H ₂ O.....	1:20
Mn ⁺⁺ ,	Manganese,	MnCl ₂ .4H ₂ O.....	1:50
Hg ⁺⁺ ,	Mercuric,	HgCl ₂	1:50
Hg ⁺ ,	Mercurous,	HgNO ₃ *.....	1:50
Ni ⁺⁺ ,	Nickel,	NiCl ₂ .6H ₂ O.....	1:50
K ⁺ ,	Potassium,	KCl.....	1:20
Na ⁺ ,	Sodium,	NaCl.....	1:20
Ag ⁺ ,	Silver,	AgNO ₃	1:50
Sn ⁺⁺⁺⁺ ,	Stannic (Tin),	SnCl ₄ (or with SnBr ₄) †.....	1:50
Sn ⁺⁺⁺ ,	Stannous (Tin),	SnCl ₂ .2H ₂ O ‡.....	1:50
Sr ⁺⁺ ,	Strontium,	SrCl ₂ .6H ₂ O.....	1:20
Zn ⁺⁺ ,	Zinc,	ZnSO ₄ .7H ₂ O.....	1:50

* Dissolve the metal in an excess of cold dilute nitric acid, and dilute to the proper strength.

† Add chlorine-water or bromine in slight excess to a solution of stannous chloride.

‡ This solution should be acidified with hydrochloric acid, and some fragments of metallic tin should be put into the bottle.

CHAPTER II.

GROUP A. (FRESENIUS'S GROUP V, DIVISION I.)

RADICALS WHOSE CHLORIDES ARE INSOLUBLE OR NEARLY INSOLUBLE IN ACIDIFIED SOLUTIONS.

1. FIND by experiment which of the 27 solutions give precipitates when a few drops of hydrochloric acid, HCl , are added to 1 or 2 cc in a test-tube. Write the equations of the reactions, and remember the facts observed in this experiment as well as in those that follow. Why are no precipitates produced in the solutions containing chlorides?

2. Take a measured quantity, about 5 cc, of each solution in which hydrochloric acid produces a precipitate, dilute it to ten volumes with distilled water, keeping the apparatus perfectly clean so that the solution will not become contaminated with any other substance, mix the diluted liquid thoroughly, and add hydrochloric acid to a small portion as before. Clean the measuring-cylinder with distilled water, and dilute some of the last solution ten times in the same way, calculating from the original strength of the solutions how much solid salt is present, then go on testing and diluting in the same manner until the reaction disappears. From this experiment, in the case of each of the metals, decide whether or not the precipitation by hydrochloric acid is practically complete.

3. To learn the process of analysis, take separately in small beakers 5 or 10 cc of the three solutions which give precipitates with hydrochloric acid, and in another beaker

make a mixture of about the same quantities of these solutions. Label the beakers accurately, and in all subsequent operations take care that no mistakes in the identity of the substances are made.

. To each solution, diluted slightly with water, add hydrochloric acid gradually, with stirring, until no further precipitation is evident. Agitate thoroughly by stirring, filter through small filters into clean beakers, and add a little hydrochloric acid to the filtrates to make sure that enough has been used. These filtrates (which, in the case of a complete analysis, would be examined for the other groups) may be thrown away if they give no precipitate with hydrochloric acid.

Treat the chlorides in the four filters with boiling water, and in each case catch the liquid which runs through, in a clean test-tube. To the liquid from the mixed chlorides add a considerable quantity of dilute sulphuric acid, H_2SO_4 . Find which of the metals has given the reaction, by adding sulphuric acid in the same way to the liquids from the separate chlorides. Add sulphuric acid to a portion of the original solution of the nitrate of this metal, allow some of the precipitate to settle, pour off the liquid, and see if the precipitate dissolves in hot water like the chloride.

Continue the application of hot water to the chlorides on the filters until sulphuric acid fails to give any precipitate in the washings, then upon all the filters pour ammonium hydroxide, NH_4OH , diluted with two or three volumes of water, catching the liquids in clean test-tubes. Notice any change of color taking place, and from the single chlorides decide which metal it is that gives the reaction.

Acidify the ammoniacal solutions in the test-tubes with nitric acid, and decide which metal it is that gives this reaction. By experiment find if nitric acid gives a precipitate in solutions of the nitrate of this metal. Can the precipitate be the nitrate of the metal?

Mix a few drops of a solution of silver nitrate with a dilute solution of hydrochloric acid. To a little of this turbid liquid add about ten volumes of hydrochloric acid, and warm. Warm another portion with ten volumes of nitric acid, and from the results decide why nitric acid rather than hydrochloric acid was used for acidifying the ammoniacal solution in the analysis.

Continue to treat the black residue resulting from the mixture of chlorides, with dilute ammonium hydroxide, taking care to wash the upper edge of the filter thoroughly, until the washings give no more than a faint turbidity upon being acidified with nitric acid. Then remove the filter from the funnel, unfold it, tear off and throw away all the paper except the part to which most of the black substance adheres, place the latter in a clean test-tube, add a few drops of hydrochloric and nitric acids, and warm gently, adding more of the acids if necessary, until the black substance has turned nearly white. Dilute the aqua regia with several volumes of water, transfer to a filter the fragments of filter-paper with whatever may adhere to them, and wash thoroughly with water. Treat the black residue resulting from a single chloride in exactly the same way. Place clean test-tubes under the funnels containing the shreds of filter-paper, treat the latter with dilute ammonium hydroxide, and acidify the liquids with nitric acid.*

Analyze unknown solutions of this group. At least three correct analyses should be made.

* The black residue retains a certain amount of silver in such a form that it does not dissolve in ammonium hydroxide. When mercurous chloride is mixed with a comparatively small quantity of silver chloride, it frequently happens that none of the latter is dissolved by ammonia, and it is not detected unless the supplementary operation is performed. It is evident that this search is unnecessary if silver has been found.

CHAPTER III.

GROUP B. (FRESENIUS'S GROUP V, DIVISION II.)

RADICALS (EXCEPTING Ag^+ AND Hg^+) WHOSE SULPHIDES ARE PRECIPITATED IN ACID SOLUTIONS, AND ARE INSOLUBLE IN YELLOW AMMONIUM SULPHIDE.

1. FIND by experiment which of the 27 solutions, after being acidified, give precipitates with a liberal amount of hydrogen sulphide, H_2S , water. Use hydrochloric acid for acidifying, except where this would produce a precipitate, and in the latter case use nitric acid. Notice the colors of the precipitates carefully, and in the case of the mercuric chloride solution, repeat the experiment, adding the hydrogen sulphide water very gradually, mixing well, and finally using an excess. In the cases where precipitations have occurred (with the exception of the ferric solution, which gives a precipitate of sulphur) take separately, in labeled test-tubes, 2 or 3 cc of the liquids in which the precipitates are suspended, add a little ammonium hydroxide until the acid is neutralized, then add several volumes of yellow ammonium sulphide,* $(\text{NH}_4)_2\text{S}_{1+x}$, warm gently, adding more yellow ammonium sulphide if partial solution appears to have occurred, and thus determine which sulphides are insoluble in the ammonium sulphide.

* If the ammonium sulphide at hand is not distinctly yellow in color, a little powdered sulphur should be dissolved in it. The action of the air also gradually changes the color of the solution: $(\text{NH}_4)_2\text{S} + \text{O} = 2\text{NH}_3 + \text{H}_2\text{O} + \text{S}$.

2. Determine the delicacy of the reaction with hydrogen sulphide in one or two of the cases where this produces a precipitate, by making the experiment with systematically diluted solutions.

3. To separate solutions of silver and lead add hydrochloric acid as long as a precipitate forms, but not in large excess. Shake well and filter into clean test-tubes. To the filtrates add a little hydrochloric acid to make sure that enough has been used, re-filter them if they are not perfectly clear, and add hydrogen sulphide water to them. What inference may be drawn from the results?

4. To learn the process of analysis, take separately, in rather large beakers, about 10 cc each of solutions of the radicals which give sulphides in acid solutions and whose sulphides are insoluble in yellow ammonium sulphide, omitting the silver and mercurous radicals, which are completely precipitated in the preceding group. In each case dilute to about 100 cc with distilled water, and add about 5 cc of hydrochloric acid. If, in the bismuth solution, there is a precipitate of basic bismuth nitrate or chloride, $\text{Bi}(\text{OH})_2\text{NO}_3$, or BiOCl , add enough hydrochloric acid to dissolve it.* If there is a precipitate of lead chloride in the lead solution, allow it to settle, then pour off and use the clear liquid, since enough lead chloride for the purpose will remain in solution. Make a mixture of all the five solutions, adding the lead solution last, after diluting largely and dissolving any basic bismuth nitrate in hydrochloric acid. Finally pour off or filter from any precipitated lead chloride.

Into all the solutions, while cold,† pass a slow stream of

* It is not absolutely necessary to use a clear solution, because this precipitate (and precipitated lead chloride also) is changed to sulphide readily by the action of hydrogen sulphide.

† The solutions should not be heated when nitrates are present, because these with hydrochloric acid make aqua regia, and this prevents the precipitation of the sulphides, especially when warm. Nitric acid alone, unless extremely dilute, prevents the precipitation in most cases.

hydrogen sulphide gas until the precipitation is apparently complete. Filter into clean beakers, and *test the filtrates* by adding a liberal amount of hydrogen sulphide water. If a further precipitation takes place (in the case of the mixture, at least) hydrogen sulphide must be passed into the solution again, and the precipitate collected with the rest, because, when there is a partial precipitation, some of the metals may not be precipitated at all. When the filtrates give no reaction with hydrogen sulphide water, they may be discarded, since other groups are not considered here. *

Wash the precipitates with hot water until, in each case, a few drops of the washings remain clear upon the addition of a drop of silver nitrate solution together with a drop of nitric acid, thus showing that all the hydrochloric acid and other chlorides have been washed out. This thorough washing is indispensable, as will be explained beyond, and it can be accomplished quickly if the stream from the wash-bottle is frequently directed around the whole upper edge of the filter, which should never extend to the top of the funnel.

When the washing is complete, with a pointed glass rod pierce a hole in the apex of the filter containing the mixture of sulphides, and wash most of the precipitate down into a casserole, employing a small jet of water from the wash-bottle, and using no more water than necessary. Add to the casserole about as much nitric acid (pure dilute) as there is water present, and heat to boiling for a few moments, but do not evaporate far.† Filter off the undissolved residue, preserving both residue and filtrate.

especially when hot. Even hydrochloric acid, if the solution is too hot or concentrated, prevents the precipitation of some of the sulphides.

*The great importance of always testing the filtrates from these sulphides with a liberal quantity of hydrogen sulphide *water* should not be overlooked. It often happens that the liquid contains so much acid that the *gas* cannot produce a complete precipitation; but the water is a decisive test, because it dilutes the liquid sufficiently, especially if it is added in a layer upon the top of the liquid to be tested.

† Too strong nitric acid is liable to oxidize sulphur to sulphuric acid,

Treat the separate sulphides with hot dilute nitric acid, in exactly the same way, saving the part containing the metal in each case.

Dissolve the black residues (left by treating the mixed sulphides and the separate sulphides with hot dilute nitric acid) by heating them with a small volume of hydrochloric acid to which a little nitric acid is added (aqua regia).^{*} Do not boil too long, because the chloride of this metal gradually volatilizes with steam. Filter, if necessary, and add stannous chloride, SnCl_2 (the strong solution used as a reagent), to the liquids. Make experiments with the original solutions of the metals of this group and stannous chloride. If a precipitate is produced in the cupric solution (white cuprous chloride, CuCl), it will be noticed that hydrochloric acid will prevent its formation.

To the solution containing the mixture of metallic nitrates add about 20 cc of dilute sulphuric acid, and evaporate the liquid by hand over the flame until fumes of sulphuric acid begin to come off.[†] These fumes are recognized by the facts that they are very dense and white, and that, while they do not possess any marked odor, they always produce coughing when a small quantity is inhaled.

Perform the foregoing operation with the solutions produced by dissolving the separate sulphides in hot nitric acid.

and this precipitates lead sulphate, which is nearly insoluble in nitric acid. Long boiling with strong nitric acid converts mercuric sulphide into a white, insoluble body, $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$. This is the same compound as the white precipitate produced by adding a small quantity of hydrogen sulphide to a solution of mercuric nitrate, and is analogous to the white precipitates obtained in the same way with solutions of other mercuric salts.

^{*} When it is known that mercuric sulphide dissolves in aqua regia, the reason for thoroughly washing the original precipitate of sulphides is evident, for if hydrochloric acid or other chlorides remained in the precipitate, aqua regia would be formed when it was treated with nitric acid.

[†] The removal of the nitric acid by evaporation is necessary, because lead sulphate is somewhat soluble in that acid.

In each case, after the sulphuric acid has become cold, add to the casserole a mixture of about 10 cc of dilute sulphuric acid and 50 cc of water, warm gently to dissolve soluble sulphates, and transfer the liquid to a beaker, in order to detect any undissolved residue that it may contain. In the cases where residues remain, filter the solutions without delay.*

To the filtrate containing the sulphates of copper, cadmium, and bismuth, as well as much sulphuric acid, add ammonium hydroxide in considerable excess beyond the amount necessary to neutralize the acid. Heat nearly to boiling, filter, and save both precipitate and solution. Perform the same operations with the solutions of the sulphates of the separate metals, in order to determine which gave the color and the precipitate.

With hot water wash the white precipitates produced by ammonium hydroxide, and pour upon them a little sodium stannite solution, Na_2SnO_3 ,† which is prepared by taking 2 or

* Where large amounts of bismuth are present, it may be advisable to let the residue settle, pour or filter off the liquid, and evaporate again after adding a fresh portion of sulphuric acid to the residue. This is in order to be certain that the residue is not a basic bismuth sulphate. If sufficient sulphuric acid is used, and the liquid is not diluted too far or is not allowed to stand too long, no basic bismuth sulphate can be formed.

† If any mercuric or mercurous compound were present here, a black coloration, due to finely divided metallic mercury, would be produced by the action of sodium stannite; but if the analysis has been properly conducted, no more than a trace of any mercury compound could be present at the point where the sulphuric acid solution was made ammoniacal, and, even if present, it would not be precipitated by ammonium hydroxide under the existing conditions. Another method of testing the precipitate produced by ammonium hydroxide (which, although not as delicate as the one which has been given, is not interfered with by the presence of mercuric salts), is carried out as follows: Dissolve the precipitate in the smallest possible quantity of dilute hydrochloric acid. To do this, remove the precipitate from the filter with a spatula, or, if the amount is small, tear off the paper to which most of it adheres, place it in a small dish, and add a drop of hydrochloric acid at a time, with a few drops of water, until the precipitate dissolves. If too much hydrochloric acid is used, the subse-

3 cc of stannous chloride solution in a test-tube, and gradually adding sodium hydroxide solution until the liquid is strongly alkaline, and the precipitate formed at first has redissolved.

Boil the ammoniacal solution containing copper and cadmium until the greater part of the ammonia has been removed, then add hydrochloric acid cautiously, in *slight* excess. Cool the solution, and pass in hydrogen sulphide until the precipitation is apparently complete. Filter off the precipitate, and *do not neglect to test the filtrate* with a liberal amount of hydrogen sulphide water, since cadmium sulphide precipitates last and may be missed at this point. Perform the same operations with the ammoniacal solutions containing copper and cadmium separately.

Wash with water two or three times the precipitate containing the two sulphides, transfer it by means of a little water to a test-tube, and add small pieces of solid potassium cyanide, KCN (Poison!), with warming until no further action is evident.* Filter off the precipitate, wash it well, and boil it in a test-tube with dilute sulphuric acid. Filter, if necessary, and add a large amount of hydrogen sulphide water to the solution. Apply the above process to the separate sulphides.

Analyze unknown solutions containing these metals.

quent reaction will not appear unless the excess is removed by evaporation to extremely small bulk. Pour or filter this solution of the precipitate in hydrochloric acid, into a large beaker nearly full of distilled water.

* The precipitate at this point may not show its characteristic yellow color on account of the presence of traces of black sulphides (possibly mercuric and lead sulphides) which are insoluble in potassium cyanide solution. In this case, the subsequent boiling of the precipitate with dilute sulphuric acid dissolves the yellow sulphide, and leaves the black sulphides undissolved. The method of testing for cadmium sulphide in the presence of copper sulphide may be modified by omitting the use of potassium cyanide, and at once boiling the mixture of the two sulphides with dilute sulphuric acid, filtering, and testing the filtrate with hydrogen sulphide water. This modification would be preferable were it not that the potassium cyanide method usually gives a decisive result directly.

CHAPTER IV.

GROUP C. (FRESENIUS'S GROUP VI.)

RADICALS WHOSE SULPHIDES ARE PRECIPITATED IN ACID SOLUTIONS, AND ARE SOLUBLE IN YELLOW AMMONIUM SULPHIDE.

1. THE radicals under consideration have been identified in Chapter III, 1. Prepare the sulphides again, noticing their colors, dissolve them in yellow ammonium sulphide according to the directions given for the course of experiments just referred to, acidify the liquids slowly, under the hood, with hydrochloric acid, and, for comparison, acidify a similar quantity of yellow ammonium sulphide by itself. Observe and explain the change in color of the final precipitate where stannous sulphide was used.

2. To learn the process of analysis, take separate and mixed solutions containing the radicals in question, and treat each of the five solutions according to the following directions:

Precipitate with hydrogen sulphide gas in a cold dilute solution, just as in the preceding group, filter, and test the filtrate with hydrogen sulphide water.* Wash the precipitate somewhat (complete washing is unnecessary here because the other groups are not present), remove it to a casserole, and add yellow ammonium sulphide, heating to boiling, until the precipitate dissolves. To the solution containing ammonium thioarsenate, ammonium thiostannate, and ammonium thioantimonate, or one of these compounds, and an excess of yellow ammonium sulphide, add hydrochloric acid gradually,

* Heat should be also applied where arsenic acid, H_3AsO_4 , may be present.

with stirring, until the liquid is acid and effervescence ceases, then collect the resulting precipitate upon a filter.*

Wash the precipitate (best with hot water) and transfer it by means of a small volume of water to a small glass flask. Add a volume of concentrated hydrochloric acid equal to the volume of liquid in the flask, and boil the liquid until a strip of filter-paper moistened with lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, solution, and held in the escaping steam, is no longer blackened quickly or to a marked extent.† Stop the boiling promptly when the hydrogen sulphide reaction ceases, filter, and save both residue and solution.

Wash the residue left undissolved by boiling hydrochloric acid (best with hot water) until silver nitrate gives no turbidity in the washings. This thorough washing is necessary. Do not add these washings to the filtrate, since they would dilute it inconveniently.

Transfer the washed residue to a test-tube, using very little water for the purpose, add as much concentrated nitric acid as there is water, and boil until red fumes are no longer given off, even upon adding a little more concentrated nitric acid and boiling. Add a considerable quantity of silver nitrate solution, boil, and filter off any small precipitate of silver chloride which usually forms in spite of the previous thorough washing, collecting the liquid in a clean test-tube. Add a little more silver nitrate if the precipitate of silver chloride was large, as it is necessary that there should be an excess of silver present. Nearly neutralize the liquid in the test-tube with ammonium hydroxide, stirring it, and leaving it acid to test-paper, or, if too much ammonium hydroxide

* The operation of dissolving the sulphides in yellow ammonium sulphide and reprecipitating with hydrochloric acid is superfluous, unless sulphides are present which are thus separated from this group. This step, therefore, may be omitted in actual analysis when Group B is absent.

† Paper moistened with an alkaline lead solution is too delicate for this test, since the sulphides of arsenic continually give off traces of hydrogen sulphide when treated in this manner.

has been accidentally added, acidify carefully with nitric acid. Cool the liquid, and finally, by careful addition of ammonium hydroxide, make the top of the liquid in the test-tube slightly alkaline, while that in the bottom remains acid. Under these conditions, there must be a neutral zone between the acid and alkaline liquids in the test-tube. This zone may be widened by cautious stirring.

Boil down the solution obtained by boiling the sulphides with hydrochloric acid, to small bulk in a casserole, in order to remove most of the hydrochloric acid, but not to dryness, since this might cause the volatilization and consequent loss of the chlorides present. Add a little water, place a piece of platinum foil in the liquid, and upon it a piece of metallic zinc. Any change in the appearance of the foil should be noticed. Heat the liquid, adding more zinc if the first piece becomes small, and allow the action to continue until the evolution of hydrogen has practically stopped, then pour off the liquid and discard it, leaving the residue. Take out the solid zinc as far as practicable, rubbing it, and washing back into the casserole any loose, adhering matter, then allow the residue to settle, and pour off and throw away the water that has been used.

Add about 10 cc of hydrochloric acid to the residue, and heat until effervescence of hydrogen ceases. Do not boil too long, because this would cause the oxidation of the chloride present in solution, and the subsequent reaction might not appear. Filter the solution into a test-tube, and add mercuric chloride solution.

Completely wash the black residue adhering to the foil or left in a loose condition, by repeated decantation with water, warm it with a few drops of nitric acid, adding a little tartaric acid, if necessary, to dissolve it. Add hydrogen sulphide water to the solution, noticing the color of the precipitate.

Analyze unknown solutions of this group.

CHAPTER V.

GROUP D. (FRESENIUS'S GROUP III AND IRON.)

RADICALS NOT INCLUDED IN THE PRECEDING GROUPS, WHOSE HYDROXIDES ARE PRECIPITATED IN THE PRESENCE OF AMMONIUM CHLORIDE BY AMMONIUM HYDROXIDE.

N.B.—These hydroxides may combine with, and cause the partial or complete precipitation of, hydroxides of the bivalent radicals of the subsequent groups (E, F, and magnesium in G). Moreover, many of the bivalent radicals just mentioned may be precipitated by ammonium hydroxide, from acid solutions containing the phosphate, oxalate, borate, silicate, and fluoride radicals, because their phosphates, etc., in many cases, are insoluble in neutral or alkaline solutions.

1. To solutions of each of the radicals not belonging to the preceding groups, add one or two volumes of ammonium chloride, NH_4Cl , solution (the 1 : 10 solution used as a reagent), then add ammonium hydroxide in distinct excess, and boil. For convenience in boiling in a test-tube, use small volumes and keep the liquid continually agitated. Be sure that the resulting precipitates will not dissolve upon the addition of more ammonium chloride. Notice that a precipitate forms in the ferrous solution, and gradually increases on standing, owing to the fact that the ferrous salt is oxidized to a ferric salt by the action of the air. Notice also that a slight precipitate usually forms in the manganese solution when it is made alkaline with ammonium hydroxide and boiled.

This is a higher oxide of manganese, and is also due to the action of the oxygen of the air, or to that which is dissolved in the liquids used. From these appearances, do not be led to the conclusion that the ferrous and manganese radicals are precipitated by ammonium hydroxide in the presence of ammonium chloride.

2. Find an explanation for the use of ammonium chloride in the preceding experiments, by repeating them in the cases of manganese and magnesium, without using the reagent under consideration. From the equations notice that ammonium salts are produced in the reactions, and therefore that these precipitations cannot be complete.

3. To manganese, magnesium, barium, strontium, and calcium solutions (in which ammonium hydroxide with ammonium chloride gives no precipitates), add a little sodium phosphate, HNa_2PO_4 , solution, and add hydrochloric acid until the precipitate dissolves, then to each add ammonium chloride and ammonium hydroxide in excess. Observe that, in the presence of a phosphate, certain metals are precipitated by ammonium hydroxide, which would not be precipitated if the phosphate were absent.

4. To separate solutions of ferrous sulphate, FeSO_4 , (remembering that it contains a little ferric salt from the action of the air), and ferric chloride, FeCl_3 , add potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, solution. To fresh portions of the same solutions add the same reagent after having passed hydrogen sulphide into them until they smell distinctly of the gas after the air above the liquid has been blown away. Inference?

5. To separate solutions of ferrous sulphate and ferric chloride add potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, solution (prepared by dissolving a very little of the solid salt in water—the solution does not keep well). Boil fresh portions of the two solutions with enough aqua regia (hydrochloric and nitric acids) to give an odor of chlorine, dilute somewhat, and to a part of each add potassium ferrocyanide solution. To the

other part add potassium ferricyanide solution. Inference?

6. To learn the method of analysis *when the subsequent groups need not be considered (Case I)*,* take in rather large beakers separate and mixed solutions of the three radicals which belong to this group, and also take a ferrous solution separately and in the mixture. Carry out the following operations in each case:

Add a few cc of nitric acid and boil. What change takes place in any case? Add a considerable amount of ammonium chloride, dilute rather largely, heat to boiling, and add ammonium hydroxide until its odor prevails on further boiling, but not a large excess. Filter while hot (best through a plaited filter) and wash the precipitates once or twice with hot water. The filtrates can be rejected, since other groups are not considered.

Boil the precipitates with at least their own volume of sodium hydroxide or potassium hydroxide solution, filter, and save the filtrates and residues. Acidify the liquids with hydrochloric acid, testing with litmus-paper to be sure that

* This method may be applied, however, even when the subsequent groups are to be considered, if it is known that chromium, phosphates, borates, oxalates, silicates, and fluorides are absent, and if it is not necessary to test for relatively small quantities of the bivalent metallic radicals of the subsequent groups. Chromium hydroxide has a strong tendency to combine with the hydroxides of the bivalent radicals just referred to, and may cause their complete precipitation. The presence of chromium is usually revealed by the color of the solution under examination. The phosphates, oxalates, etc., of bivalent metallic radicals cannot be present with Group D if the original solution had a neutral reaction, because they are insoluble in water. The silicate radical may be removed by evaporating the acidified solution to complete dryness, and treating the residue with hydrochloric acid, when silicic anhydride, SiO_2 , remains undissolved. By evaporating the solution to dryness and heating the residue to the point at which organic matter is charred, oxalic acid may be destroyed, and the residue may then be dissolved in hydrochloric acid. It should be noticed that many non-volatile organic substances, such as tartaric acid, citric acid, sugar, etc., prevent the precipitation of the hydroxides of this group (D), and, if present, such organic matter should be destroyed by heating.

the solution is acid, then add a slight excess of ammonium hydroxide, and if no precipitate is formed at once, heat to boiling.*

Boil the residues left undissolved by sodium or potassium hydroxide, with solution of sodium hypochlorite, NaClO (containing sodium hydroxide), filter, and observe the color.†

The ferrous and ferric radicals must be detected in an original solution to which no nitric acid, hydrogen sulphide, etc., have been added. Why? Compare the behavior of original ferrous and ferric solutions with ammonium thiocyanate, NH_4CNS , potassium ferrocyanide, and potassium ferricyanide solutions.

7. To follow the process of analysis *when the subsequent groups must be taken into consideration (Case II)*,‡ make a mixture of the three solutions containing the radicals of this group, and add a ferrous salt to it, as in Case I. Make another solution by mixing calcium chloride, magnesium chloride, and manganese chloride solutions with rather large amounts of sodium phosphate and ammonium oxalate solutions, and adding hydrochloric acid until the resulting precipitate dissolves.

Make a mixture of rather small quantities of the two solutions that have thus been prepared, and in another beaker take a portion of the second (phosphate and oxalate) solution. These will serve as examples of the substances that may be encountered in this case. Subject them to the following operations:

* Since sodium or potassium hydroxide solution is often impure, it is well to take the same quantity of this reagent by itself, and after acidifying it with hydrochloric acid, adding a small excess of ammonium hydroxide and boiling, to compare the quantity of the precipitate thus produced (if any) with that produced in the actual test.

† When Group D has been separated from Group E, it often happens that a little manganese present here gives a red solution due to sodium permanganate. This may be destroyed without affecting the yellow color under consideration, by the addition of a little alcohol, and boiling.

‡ See foot-note, p. 19.

Add nitric acid and boil, dilute somewhat, add ammonium chloride, precipitate hot with ammonium hydroxide, filter, and wash, exactly as in Case I. Consider what the precipitate in the phosphate and oxalate solution may contain, and notice that the other precipitate must contain the same compounds. The addition of ammonium sulphide and ammonium carbonate (the reagents used to precipitate groups E and F) may or may not give precipitates in these filtrates, according to whether an excess of sodium phosphate (and ammonium oxalate) was added. After making this test, these filtrates may be discarded, as the subsequent groups are not specially examined in these experiments.

Dissolve the precipitates upon the filters with hot hydrochloric acid, avoiding an unnecessary volume, and collect the solutions in casseroles. Add a rather large quantity of ferric chloride, FeCl_3 , solution—about 25 cc of the solution used as a reagent, or more if the precipitate produced by ammonium hydroxide was large.*

Evaporate the solutions, holding the casseroles by hand over a flame, and rotating the liquid so that not much of the substance becomes dry upon the sides of the casserole during the operation, until a pasty mass is left containing but little liquid. If the evaporation has been carried so far that substances insoluble in water are left, add hydrochloric acid, and repeat the operation.

In both cases, take up the substance in a very little water (this must form a clear solution), cool it, and add sodium carbonate, Na_2CO_3 , solution drop by drop, with stirring, as long as the precipitate produced dissolves completely, and until a very slight permanent precipitate remains on long stirring. Dissolve this slight precipitate, if possible,

* If an excess of the ferric radical is present when the subsequent precipitation (by boiling the dilute solution with sodium acetate) is made, the phosphate and oxalate radicals will combine with it in preference to the bivalent metals, and the latter will remain in solution and thus be separated from the acid radicals mentioned.

with a *single drop* of hydrochloric acid; but in any case use as little hydrochloric acid as possible to obtain a clear solution. It is indispensable that this neutralization should be very carefully performed, best in a very small volume of liquid.

In each case transfer the clear, almost neutral solution to a large flask or beaker, add 20 or 30 cc of 10 per cent sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, solution, or* more if large quantities of substances are present, dilute to 300 or 400 cc with hot water, heat, and boil for one or two minutes. On interrupting the boiling, the precipitate should settle, and leave a clear, colorless solution. If it is not colorless, add more sodium acetate, dilute with more water, and boil again. Filter while hot, best after the precipitate has subsided and without disturbing it sooner than necessary, using a plaited filter.

To the filtrates add ammonium hydroxide until they are alkaline. If the operations have been properly conducted, this will produce no precipitates. Then add ammonium chloride, ammonium sulphide, ammonium carbonate, and sodium phosphate, the reagents for groups E and F and magnesium. These solutions may now be discarded, but in a general analysis for all the groups, they would be systematically analyzed for all the metallic radicals of the subsequent groups, excepting the alkali metals. Since a sodium salt (which interferes with the detection of sodium and the other alkali metals) has been added, these solutions would not have been mixed with the filtrates from the precipitates produced by ammonium hydroxide, in the first step of this analysis.

Test the precipitates produced by boiling the dilute solutions with sodium acetate, for aluminium and chromium by exactly the same methods as were used with the precipitate by ammonium hydroxide in Case I.*

* The presence here of phosphates and oxalates, etc., does not interfere with the test for aluminium, except in the case of silicates. Silicic acid, if present, should always be removed before this group is precipitated, by

Make analyses of unknown solutions of this group, including a ferrous salt.

evaporating the acid solution to dryness, and treating the residue with hydrochloric acid, for silicic acid dissolves in sodium or potassium hydroxide solution, and upon treating this with ammonium chloride (hydrochloric acid and ammonium hydroxide) it gives a precipitate that resembles aluminium hydroxide. Aluminium phosphate, oxalate, etc., behave with these reagents exactly like aluminium hydroxide.

CHAPTER VI.

GROUP E. (FRESENIUS'S GROUP IV, EXCEPTING IRON.)

RADICALS NOT BELONGING TO THE PRECEDING GROUPS,
WHOSE SULPHIDES ARE PRECIPITATED IN ALKALINE
SOLUTIONS BY AMMONIUM SULPHIDE.

1. TAKE in test-tubes small portions of solutions of the radicals not belonging to the preceding groups, add a rather liberal amount of ammonium chloride solution (amounting to at least one half the volume of the solution originally taken), then add two or three drops of ammonium sulphide solution.

2. *Analysis.*—In beakers of medium size, take mixed and separate solutions of the four radicals which have given precipitates in 1. In each case add a liberal amount of ammonium chloride,* make alkaline with ammonium hydroxide, avoiding a large excess, then add ammonium sulphide until, after stirring, the liquids smell distinctly of the reagent, but do not use a larger excess,† heat to boiling, filter through a plaited filter, and wash several times with water.

In general analysis, the filtrate would contain the metals of the subsequent groups, but for present purposes it may

* This is not absolutely essential here, since magnesium is absent, but it facilitates the precipitation and filtration of some of the sulphides.

† Too much ammonium sulphide, especially when an excess of ammonium hydroxide is present, causes the solution of a little nickel sulphide, forming a brown liquid. This, however, does not take place always when comparatively large amounts of other sulphides are precipitated together with the nickel sulphide, so that, although the appearance of a brown solution is a reliable test for nickel, its failure to appear does not show the absence of that metal.

be thrown away when it gives no further precipitation with ammonium sulphide.

Transfer the precipitates to beakers by means of a jet of water, using an amount of cold water (or, better, hydrogen sulphide water) several times the volume of the precipitate. In each case, add to this liquid one third its volume of cold hydrochloric acid, stir vigorously for a few moments, and filter without further delay when an undissolved residue remains.

Evaporate the solutions almost to dryness, in order to remove most of the hydrochloric acid, cool, and add cold sodium hydroxide solution in large excess beyond the point where the solution is alkaline. Filter cold, to the filtrates add a little ammonium sulphide, and heat to boiling unless a precipitate is formed at once. Fuse portions of the precipitates produced by cold sodium hydroxide, on platinum foil over the blast lamp, with a mixture of sodium carbonate and potassium or sodium nitrate, observing the color of the mass on cooling.

In the oxidizing blowpipe flame test with the borax bead small portions of the residues left undissolved by the treatment with cold dilute hydrochloric acid, noticing the color that predominates in the case of the mixture, then transfer the main parts of the residues into casseroles, dissolve by heating with a little aqua regia, and evaporate to dryness, avoiding a high heat when dryness is reached. Take up the residues in a very little water, perhaps 4 or 5 cc, and transfer the solutions to test-tubes. In each case add a volume of solid potassium nitrite, KNO_2 , equal to at least half the liquid in the test-tube. When this has dissolved, add 1 or 2 cc of acetic acid gradually, with shaking, heat nearly to boiling, and keep in a moderately warm place for several hours. Filter off the yellow precipitates, and when the filtrates give no further precipitation upon the addition of more potassium nitrite and acetic acid, and warming for an

hour or more, add an excess of sodium hydroxide, boil, and filter off any precipitates that form.

Test these precipitates, as well as the yellow precipitate produced by potassium nitrite, in the borax bead in the oxidizing flame before the blowpipe.

Compare the reactions of nickel, cobalt, and iron, in the borax bead before the blowpipe, ascertaining if either cobalt or nickel hides the reaction of the other. Use solid salts for these experiments.

Test the behavior of solutions of all the metals of groups D and E when sodium hydroxide solution is added in excess, cold, and afterwards boiled.

Make analyses of unknown solutions of this group.

CHAPTER VII.

GROUP F.

(FRESENIUS'S GROUP II, EXCEPTING MAGNESIUM.)

RADICALS NOT BELONGING TO THE PRECEDING GROUPS,
WHOSE CARBONATES ARE PRECIPITATED BY AMMONIUM
CARBONATE IN THE PRESENCE OF AMMONIUM CHLORIDE
IN ALKALINE SOLUTIONS.

DETERMINE which are the three radicals belonging to this group, and find the reason for the use of ammonium chloride, by repeating the experiment without adding that reagent in the cases where no precipitate has been produced.

In rather small beakers, take mixed and separate solutions of the three radicals under consideration and of magnesium (the last is used for the sake of showing distinctly its separation from the others), add ammonium hydroxide to alkaline reaction, then add ammonium chloride, using enough, in the cases where a precipitate has formed, to dissolve the latter. Add ammonium carbonate as long as a precipitate forms, heat to boiling, and filter hot where precipitates are obtained, collecting the filtrates in clean beakers.

After ascertaining that ammonium carbonate gives no further precipitate, divide all these filtrates and also the solution which gave no precipitate, into two parts, to one of which, in each case, add a little ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, solution, and to the other a few drops of ammonium sulphate solution, made by neutralizing a little sulphuric acid with

ammonium hydroxide. Observe any precipitates that occur, and in all cases unite the two parts that were previously separated. Mix thoroughly in the cases where there are precipitates, and filter them off, noticing what they are. To each of the five solutions add some sodium phosphate, HNa_2PO_4 , solution, and then one half its volume of ammonium hydroxide.

To small quantities of original solutions of all the metals under consideration apply the test with sodium phosphate and ammonium hydroxide, and ascertain the reason why calcium and barium are so carefully removed in making the analysis. In the case of magnesium test the delicacy of this reaction, rubbing the inner surface of the test-tube with a glass rod, in order to induce precipitation in dilute solutions.

Dissolve the precipitated carbonates upon the filters with hydrochloric acid and water, catch the solutions in casseroles, and evaporate them to dryness to remove all the hydrochloric acid.

Dissolve the dry residues in water, add a liberal amount of sodium acetate solution, heat to boiling, and add potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, solution in excess. Filter hot where precipitates are produced, and add more sodium acetate and potassium dichromate to the filtrates, to make sure that enough has been added.

In the case where a precipitate was produced in the solution of a *single* metallic radical, add a few drops of sulphuric acid to the filtrate. Test the delicacy of the sulphuric acid reaction with original solutions of the three metallic radicals of this group, and decide whether or not the precipitation of the chromate was complete.

To the other filtrate containing two of the metallic radicals, and to the two solutions of single metallic radicals in which potassium dichromate did not produce a precipitate, add ammonium hydroxide and ammonium carbonate in excess, boil, filter, and wash until the precipitates and paper

are entirely free from yellow chromates. This washing is necessary; otherwise chromates instead of nitrates will be obtained in the next operation.

With nitric acid dissolve the three washed precipitates of carbonates upon the filters, catch the liquids in casseroles, evaporate to dryness, avoiding a high heat beyond that point.

By the aid of heat dissolve the nitrates in the least possible amount of water, transfer the liquids to test-tubes, boil off the water until salts begin to crystallize out, or until only a few drops remain, add about 10 cc of amyl alcohol, drop in a coil of small platinum wire, and boil cautiously * under the hood until the aqueous liquid at the bottom disappears. Then add enough amyl alcohol to make a volume of about 15 cc and a drop of nitric acid, and cautiously boil down the liquids to about one half their volume, in order that the amyl alcohol may become anhydrous. Filter hot through perfectly dry filters (because water would dissolve the precipitated salt), catching the filtrates in casseroles.

Evaporate or burn off the amyl alcohol from these filtrates, take up the residues with water, filter if necessary, and add ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, solution to the liquids.† Make experiments with ammonium oxalate, and the original solutions of the metals of this group, testing the delicacy of the reaction.

* The test-tube must not be pointed so that its contents may be thrown out upon the operator or other persons. It is best to agitate the contents of the test-tube while being heated, holding it by means of a suitable test-tube holder. The amyl alcohol may ignite at the mouth of the test-tube, but this does not interfere with the process, and the flame may be readily blown out upon interrupting the boiling.

† If the residue left upon evaporation is extremely small, in order to avoid mistaking a trace of strontium nitrate possibly present, for calcium nitrate, it may be best to follow the method given in Fresenius, near the bottom of p. 160, viz.: Take up the residue in about 4 cc of water, add about 1 g of solid ammonium sulphate and a few drops of ammonium hydroxide, heat to boiling, filter through a small filter, add to the filtrate a drop of acetic acid, so that it just reddens litmus-paper, then a few drops of ammonium oxalate.

Test small portions of the residues left undissolved by amyl alcohol (after having washed them two or three times with small volumes of the amyl alcohol) by introducing them into the Bunsen flame on a clean platinum wire. In each case dissolve the remainder in water, boil the solution for a short time in order to remove traces of amyl alcohol, and add potassium sulphate, K_2SO_4 , solution. Make experiments with the flame colors produced by salts of metals of this group, using solid salts. Make experiments with potassium sulphate and the original solutions of this group.

Analyze unknown mixtures of the metals of this group and magnesium.

CHAPTER VIII.

GROUP G. (FRESENIUS'S GROUP I AND MAGNESIUM.)

RADICALS NOT BELONGING TO THE PRECEDING GROUPS.

TAKE separate solutions of the five radicals not belonging to the preceding groups, and a mixture of all of them in small beakers. Add some ammonium chloride and a few drops of ammonium oxalate and ammonium sulphate to each of them (to imitate the conditions existing after removing traces of calcium and barium), and to a *portion* of each add sodium phosphate and half its volume of ammonium hydroxide. This cannot be added to the whole, because a sodium salt would be introduced.

Evaporate the remainder of each solution to dryness in a casserole, transfer the residue to a small porcelain crucible, and heat not above low redness until white fumes stop coming off.* In one case no residue will be left.

Take up the residues with small quantities of water and transfer to beakers, and (whether the solution is complete or not) add barium chloride as long as a precipitate forms, and then add barium hydroxide in excess, boil and filter, saving the filtrates. These filtrates should become turbid on exposure to the air, owing to the formation of barium carbonate, if enough barium hydroxide has been added and an excess is present. Experiment with barium hydroxide and portions

* If the residue is heated too long or too intensely, the chlorides of sodium, potassium, and lithium, may volatilize and be lost.

of the original solutions of the salts of the metals under consideration.*

To the filtrates containing barium hydroxide and barium chloride (the excess added), add ammonium hydroxide and ammonium carbonate in excess, heat, and filter. Evaporate the filtrates to dryness, and heat the residues not above low redness, to drive off the ammonium chloride that has been formed. In one case no residue should be left.

Dissolve the residues in very small quantities of water, filter into test-tubes, boil off the water until salts begin to crystallize out, or until only a few drops remain, add a drop or two of concentrated hydrochloric acid, then add in each case about 10 cc of amyl alcohol and a coil of platinum wire, boil until the water disappears, add amyl alcohol to make about 15 cc and a drop of concentrated hydrochloric acid, boil off one half the liquid, and filter through a dry filter-paper, washing the residue once or twice with amyl alcohol.

Evaporate the amyl alcohol filtrates to dryness, and, in the cases where something remains, test the residue by introducing some of it into the colorless flame on a platinum wire which gives no flame coloration by itself. Make experiments with the flame coloration with all the metals of this group, noticing which of them hides the others.

In a little hot water dissolve the chlorides left undissolved by the amyl alcohol, and evaporate to dryness to remove the adhering amyl alcohol. Introduce a portion of each into the colorless gas flame. In each case dissolve the remainder in a few drops of water, and to a drop or two of this very concentrated solution add a drop of hydrochloroplatinic acid, H_2PtCl_6 solution. Experiment with hydrochloroplatinic acid

* The precipitate produced by barium chloride was barium sulphate. Ammonium sulphate was added to all the solutions, and upon ignition this displaced the other acid radicals from their salts, because it is less volatile. Sulphates cannot be converted into chlorides or nitrates by evaporation with hydrochloric or nitric acid; hence the foregoing method was used to convert sulphates into chlorides.

and solutions of salts of the metals of this group which have been concentrated by evaporation. In the cases where precipitates are produced, repeat the experiment with diluted solutions.

Moisten some dry calcium hydroxide in a mortar, with a solution of ammonium chloride, triturate, and observe the odor. Hold a rod moistened with hydrochloric acid near the mixture, and also notice the action of the escaping vapor upon moist red litmus-paper placed upon the under side of a watch-glass over the mortar. Ammonium is always tested for in a separate portion of the original substance.

Make analyses of unknown substances containing salts of the metals of this group.

CHAPTER IX.

THE SEPARATION OF THE GROUPS OF METALLIC RADICALS FROM EACH OTHER.

IT is assumed that a solution which may contain various groups of metals is to be analyzed. The treatment of solids, in order to obtain solutions of them, will be discussed in a subsequent chapter, but it should be mentioned here that when a solution contains a large amount of free acid, especially nitric acid or aqua regia, an inconveniently large dilution may be necessary before complete precipitation by hydrogen sulphide can be made. In many cases, the acid may be partly removed by concentration by evaporation, but it must be remembered that, in presence of hydrochloric acid, there may be a volatilization of arsenious chloride or possibly of mercuric chloride, and that the metals forming these chlorides may be wholly lost.

Take a sufficiently large portion of the original substance, so that the various reactions may be obtained with certainty. Avoid, however, an unduly large quantity, because this will retard the analysis on account of the time required for filtering and washing large precipitates. Very large quantities of the original substance are used for analysis only in cases where comparatively minute quantities of certain elements are to be sought.

Always reserve a considerable portion of the original solution for use in making tests for ferrous, ferric, and ammonium salts, as well as for any confirmatory tests and repetitions that may be necessary.

The Hydrochloric Acid Group (A).—To the solution, which should be cold and preferably moderately concentrated, add hydrochloric acid, with stirring, as long as a precipitate forms, and beyond this point add a small excess so as to redissolve any bismuth or antimonious oxychlorides, BiOCl or SbOCl , that may be precipitated at first under certain conditions. If no precipitate is formed, the absence of mercurous and silver salts is shown. If a precipitate is produced, the original solution having been neutral or acid, the precipitate may consist of silver chloride, mercurous chloride, and lead chloride, or one or two of these compounds. Filter it off, and analyze it according to the methods indicated in Chapter II.*

The Hydrogen Sulphide Groups (B and C).—Dilute the filtrate from the precipitation with hydrochloric acid, or the solution in which hydrochloric acid gave no precipitate, and pass hydrogen sulphide gas into the cold solution as long as a precipitate forms. Filter, and *test the filtrate with a liberal amount of hydrogen sulphide water*. Since arsenic acid, H_3AsO_4 , is very slowly and difficultly decomposed in cold dilute hydrochloric acid solution, acidify a portion of the

* If the original solution was alkaline, this precipitate may contain other substances which are soluble in alkaline solutions but not soluble in dilute hydrochloric acid. For instance, arsenious sulphide, As_2S_3 , dissolves readily in ammonium hydroxide, and hydrochloric acid added to this solution gives a precipitate of arsenious sulphide. From solutions which give off hydrogen sulphide when they are acidified, sulphides of arsenic, tin, and antimony, as well as mercuric sulphide (soluble in sodium or potassium sulphide in the presence of the hydroxide), may be precipitated; and from solutions of alkaline cyanides, certain insoluble cyanides, such as silver cyanide, AgCN , may be formed. From other alkaline solutions, the precipitate may contain silver chloride, lead chloride, lead sulphate, silicic acid, etc., as well as organic acids, such as those of soap, etc., and many compounds containing the rarer elements. So many substances may be present in the precipitate produced by hydrochloric acid in an alkaline solution, that it is best to treat it with acid solvents according to the chapter on the solution of solids for analysis, and any residue insoluble in acids according to the methods for the examination of insoluble substances.

filtrate very strongly with hydrochloric acid, warm, and pass in hydrogen sulphide. If no yellow precipitate forms after some time, it can be assumed that arsenic acid is not present in the filtrate. If it is found to be present, however, warm the whole moderately, and pass in hydrogen sulphide until it is removed.

If no precipitate has been produced by hydrogen sulphide, the absence of copper, cadmium, mercury, lead, bismuth, arsenic, antimony, and tin, is shown, except in the presence of oxalic acid, which prevents the precipitation of tin as sulphide.

If a precipitate is obtained, collect it upon a filter, and wash it with hot water until the washings give no reaction with silver nitrate. Transfer the precipitate to a casserole, add about three times its volume of yellow ammonium sulphide, heat to boiling, filter (if anything remains) and, with stirring, acidify the filtrate slowly with hydrochloric acid. If anything besides sulphur is precipitated, wash the residue, and repeat the treatment with yellow ammonium sulphide until the soluble sulphide has been completely extracted, then treat any sulphides that have remained insoluble in yellow ammonium sulphide, by the methods indicated in Chapter III.

Collect the sulphides* precipitated by hydrochloric acid in the yellow ammonium sulphide solutions, and analyze them according to Chapter IV.

The Ammonium Hydroxide Group (D).—Boil the filtrate

* Where copper is present, this precipitate will contain a little cupric sulphide, because the latter is slightly soluble in yellow ammonium sulphide. When Group C is absent, it gives a yellow color to the precipitated sulphur, although pure cupric sulphide is black. Its presence does not usually interfere with the detection of arsenic, antimony, and tin, but if the amount of copper originally present was extremely small, it may all be present here. To separate this cupric sulphide, treat the sulphides with sodium sulphide, Na_2S , solution, warming until everything but cupric sulphide dissolves, filter, and reprecipitate the other sulphides with hydrochloric acid. Sodium sulphide cannot be used for the original separation of the two groups of sulphides when mercury is present, because mercuric sulphide is considerably soluble in this reagent.

from the hydrogen sulphide precipitate, or the solution in which it produced no precipitate, until this gas is entirely removed. If sulphur has separated, filter it off, because it might be oxidized to sulphuric acid in the subsequent treatment with nitric acid, and this would cause the precipitation of barium and strontium, if they were present, in the form of sulphates.

If iron is present (since it must have been in the ferrous condition in a solution that has been treated with hydrogen sulphide) add some nitric acid, and boil, in order to convert ferrous into ferric salts.*

* At this point, non-volatile organic matter, which may entirely prevent the precipitation of the hydroxides of this group by ammonium hydroxide, should be destroyed if present. It may be usually detected by evaporating a portion of the solution to dryness, and heating the residue rapidly, when the odor of burning organic matter, accompanied by charring, will occur in most cases where it is present. If organic matter is found, the whole solution to be analyzed should be treated as indicated, and the heating should be continued until the burnt odor is no longer perceptible. The resulting residue should be treated with warm concentrated hydrochloric acid, and, if iron is present, the solution thus obtained should be boiled after the addition of nitric acid, since heating with organic matter may have reduced ferric to ferrous compounds.

If oxalic acid was present in the original solution, it may have prevented the precipitation of the sulphides of tin by hydrogen sulphide, and tin may be present in the solution at this point. To test for oxalic acid, take a portion of the solution that has been boiled with nitric acid, and, at a temperature a little above blood-heat, add very gradually a dilute solution of potassium permanganate, KMnO_4 . If the color disappears with the evolution of carbon dioxide, CO_2 , oxalic acid is probably present. In this case, add a slight excess of potassium permanganate to the small portion, heat to boiling with addition of hydrochloric acid, if necessary, to destroy the excess, dilute, pass in hydrogen sulphide, and test any sulphide formed, by the usual method, for tin. Do not add potassium permanganate to the main solution, as this would introduce potassium and manganese which are not yet tested for in the analysis, but destroy oxalic acid by evaporation and ignition of the residue, in the same way that other organic matter is destroyed, dissolve the residue in hydrochloric acid, remove tin, if present, by the use of hydrogen sulphide, and finally remove hydrogen sulphide; if iron is present, oxidize with nitric acid before proceeding to precipitate the ammonium hydroxide group.

If silicic acid is present, it should be removed before precipitating with

To the solution (which has been freed from organic matter, silicates, oxalates, and tin, if they were present), which must contain any iron present in the ferric state, add ammonium chloride unless there is enough free acid present to form sufficient ammonium salts upon neutralization, add ammonium hydroxide in slight excess, and heat to boiling. If no precipitate forms, aluminium, chromium, and iron are absent. If there is a precipitate, collect it upon a filter, and analyze it by the methods indicated in Chapter V. It is usually best to follow Case II in this chapter, and it must be done in any case unless it is certain that phosphoric acid is absent.

The Ammonium Sulphide Group (E).—If Case II, Chapter V, has been followed in the analysis of the preceding group, there are two solutions to be tested for the present group, which must be kept separate on account of the last group.

To the filtrate from the precipitation by ammonia, add ammonium sulphide directly, in slight excess. To the filtrate from the basic acetate precipitation, which should be concentrated by evaporation, add ammonium chloride, make slightly alkaline with ammonium hydroxide, then add the ammonium sulphide. In both cases, heat to boiling, filter separately, keeping the filtrates separate. Treat any precipitates together, in order to analyze them, according to the methods of Chapter VI.

The Ammonium Carbonate Group (F).—There may be two solutions to be tested for this group. If a solution is brown from dissolved nickel sulphide, boil it until the sulphide separates, and filter. Enough ammonium chloride is usually already present.

Add to each solution (if there are two), ammonium car-

ammonium hydroxide, by evaporating the acid solution to dryness and treating the residue with strong hydrochloric acid. Upon diluting and transferring the liquid to a glass vessel, any translucent, flocculent silica may be observed, and this should be filtered off.

bonate and also ammonium hydroxide, to make the precipitation as complete as possible. Heat to boiling, filter separately, and keep the filtrates separate. Analyze the precipitates together, as indicated in Chapter VII. Divide into two parts the separate filtrates or solutions in which ammonium carbonate has produced no precipitate, to one add a little ammonium oxalate, and to the other a few drops of ammonium sulphate in each case. Unite the divided parts, and filter if necessary.

The Soluble Group (G).—To a *portion* of the solution to which sodium acetate has not been added (perhaps one third of it), add ammonium hydroxide and sodium phosphate, allowing the liquid to stand for some time if a precipitate is not formed immediately, in order to test for magnesium. Reserve the remainder of the solution for the succeeding group. In the same way test the whole of the other solution for magnesium.

Evaporate to dryness the portion of the solution reserved when testing for magnesium, and drive off ammonium salts. If no residue remains, lithium, sodium and potassium are absent. If a residue remains, remove the sulphate radical, and magnesium if this is present (as well as any phosphate and borate radicals, etc.), by use of barium chloride and hydroxide, and proceed as indicated in Chapter VIII.

CHAPTER X.

THE INORGANIC NEGATIVE RADICALS (ACIDS).

IN the analysis of the acids, no such systematic separation into groups is made as in the case of the metals. There is one group of acid radicals, the presence or absence of which can be readily determined by the addition of silver nitrate to the nitric acid solution. However, it is not most convenient to precipitate the group in this way at the outset, because some of the tests are more easily made with soluble salts than with the silver salts. Moreover, it is not necessary in most cases to remove this group in order to test for the other acids.

The acid radicals precipitated in neutral solution as barium salts, by barium chloride solution, are not usually separated from other acid radicals by means of this reaction, because not all of them are precipitated in dilute solutions, and some are not precipitated at all in the presence of considerable amounts of ammonium salts.

It is customary, therefore, in most cases, to test for each acid in a separate portion, after removing any substances that interfere with that particular test.

The following table gives a list of the negative radicals considered in this book. Oxalates are included here (although they are salts of an organic radical) from the fact that they are of common occurrence, and because these salts do not char and give off the "burnt" odors common to other organic salts, thus failing to give the characteristic test for organic substances. The formulas of the salts that may be con-

veniently employed for the preparation of solutions for use in experiments are given, as well as the proportions of water that may be taken to dissolve these salts.

AsO ₄ '', Arsenate,	HNa ₂ AsO ₄ . 12H ₂ O.....	1:20
BO ₃ '', BO ₂ ', or B ₄ O ₇ '', Borates,	Na ₂ B ₄ O ₇ . 10H ₂ O.....	1:20
Br', Bromide,	KBr.....	1:100
CO ₃ '', Carbonate,	Na ₂ CO ₃	1:20
ClO ₃ ', Chlorate,	KClO ₃	1:20
Cl', Chloride,	NaCl.....	1:100
CrO ₄ '', Chromate,	K ₂ CrO ₄	1:20
CN', Cyanide,	KCN.....	1:20
F', Fluoride,	NaF.....	1:100
I', Iodide,	KI.....	1:100
NO ₃ ', Nitrate,	KNO ₃	1:20
C ₂ O ₄ '', Oxalate,	(NH ₄) ₂ C ₂ O ₄ . H ₂ O.....	1:25
MnO ₄ ', Permanganate,	KMnO ₄	1:100
PO ₄ '', Phosphate,	HNa ₂ PO ₄ . 12H ₂ O.....	1:20
SiO ₄ '', SiO ₃ '', etc., Silicates,	Na ₂ SiO ₃ (?).....	1:100
SO ₄ '', Sulphate,	K ₂ SO ₄	1:20
S'', Sulphide,	(NH ₄) ₂ S.....	dilute solution.*

1. To a few cc of a solution of a salt of each acid (remembering that the gas hydrocyanic acid, HCN, is a violent poison) add dilute sulphuric acid. Notice the cases where gases are given off, and detect the odors.

2. Acidify the dilute solution of a salt of each acid with dilute sulphuric acid, except in the cases where this causes effervescence, and add a liberal amount of hydrogen sulphide water. In the case of the arsenate, add also a considerable amount of concentrated hydrochloric acid, and apply heat. Notice the cases where a reaction takes place, and consider

* Dilute the solution used as a reagent with four volumes of water. Solid salts of some of these acids are also required for a few of the experiments.

which acid-forming elements would be detected in the regular analysis for the metals. The acid radicals which are reduced by hydrogen sulphide in acid solutions, and arsenic acid, will receive no further special attention among the acids.

CHAPTER XI.

GROUP A. (FRESENIUS'S GROUP II.)

ACID RADICALS WHOSE SILVER SALTS FORM PRECIPITATES IN ACID SOLUTIONS.

TAKE separate dilute solutions of salts of all the acids, add silver nitrate solution, and in each case where a precipitate results add nitric acid.

In beakers take separate and mixed solutions of salts of all the acid radicals whose silver salts are insoluble in dilute nitric acid. To each add cadmium sulphate solution, and if a precipitate forms, make a complete precipitation, and filter. It should be noticed that the sulphide radical can be removed in this way from neutral, acid, or alkaline solutions. This removal is necessary, because sulphides interfere with some of the tests that follow.

To small portions of the solutions (now containing no sulphide) add a few drops of ferric chloride solution, or at least enough to color the liquid, dissolve in each a very small fragment of crystallized ferrous sulphate, add enough sodium or potassium hydroxide to make the fluid alkaline, boil, and at last acidify the solutions with hydrochloric acid.

Acidify the remainder of each solution with acetic acid, dilute somewhat, and boil. In the cases where a cyanide is present continue this boiling for at least five minutes. During the boiling no acid stronger than acetic acid may be present. If a solution should contain a strong acid, it must be neutralized or made slightly alkaline (with sodium or potassium

hydroxide or carbonate) before adding acetic acid. On boiling an acetic acid solution iodine is not lost even in the presence of chlorates and nitrates, but it would be rapidly lost under these circumstances in the presence of a strong acid, such as sulphuric, nitric, or hydrochloric acid.

Take in test-tubes small portions of the solutions, which are now free from sulphides and cyanides, cool, acidify with sulphuric acid, add a few drops of carbon disulphide, CS_2 , then gradually, with shaking, a little potassium dichromate solution.*

To the remainder of each solution, which has been boiled after adding acetic acid, add some nitric acid, and then silver nitrate solution as long as a precipitate forms. Collect the precipitates upon filters, and wash them well with water. Make sure that the precipitation has been complete, by adding more silver nitrate to the filtrates, then reject the latter.

Be sure that the precipitates of silver salts are thoroughly washed, then place clean test-tubes under the funnels, and pour upon each precipitate 10 or 15 cc of a mixture of three volumes of ammonium nitrate solution and one volume of ammonium hydroxide.†

In each case, pour the liquid back upon the precipitate

* Another excellent indicator for free iodine is freshly prepared starch paste made by treating starch with about one hundred parts of water and boiling. Iodine may also be set free with potassium nitrite in acid solution, and with a number of other reagents which have an oxidizing action. Chlorine-water in excess forms a nearly colorless compound with iodine and bleaches iodide of starch; therefore, if it is used at all for this purpose, it must be employed with great care.

† The ammonium nitrate solution is made by exactly neutralizing ammonium hydroxide with nitric acid. The ammonium hydroxide used for the mixture should be the ordinary diluted solution of .94 sp. gr. The mixture should not be allowed to stand for any considerable time in an open vessel, since it would thus lose ammonia and become weaker. This reagent is far superior to ammonium hydroxide and water for this purpose, as the presence of ammonium nitrate greatly increases the solubility of silver chloride and bromide in ammonium hydroxide.

two or three times, catching it in a second test-tube. Take about 5 cc of the ammoniacal filtrate, in each case, and add to it an *exactly* equal volume of silver nitrate solution,* mix thoroughly by shaking, and filter off the precipitates, passing the liquids several times through the filters until they are clear, and collecting them in clean test-tubes. With nitric acid acidify the filtrates and the solution in which silver nitrate did not produce a precipitate, and observe the results.

In the preceding experiments, it has been shown that two of the silver salts are soluble in the mixture of ammonium hydroxide and ammonium nitrate. In these two cases and in the case of the mixture, add about 25 cc more of the ammonium hydroxide and nitrate mixture to the remaining liquid which has previously been passed through the filters, and continue the treatment by passing the liquid through several times, then acidify the resulting solutions with nitric acid.

Collect upon filters the precipitates produced by acidifying the ammoniacal solutions with nitric acid, wash them, transfer them to test-tubes by means of a jet of water, allow them to settle, pour off most of the water, and add some metallic zinc

* Use the regular reagent, made by dissolving 1 part of the salt in 20 parts of water. The conditions given here must be strictly followed, for if too much silver nitrate is added in proportion to the ammonium hydroxide present, all the silver chloride may be precipitated, while if too little is used, the silver bromide may be incompletely precipitated when silver chloride is absent. If the amount of silver chloride present is rather small, the addition of the silver nitrate will produce no precipitate in its ammoniacal solution, but where the ammoniacal solution is nearly saturated with silver chloride, the silver nitrate precipitates a *part* of this compound. There is no particular advantage in diluting the ammoniacal solution of silver chloride and bromide with an equal volume or more of the mixture of ammonium hydroxide and nitrate before adding an equal volume of silver nitrate solution, for it is difficult to control the conditions in such a manner that all the bromide and none of the chloride is precipitated. In fact, in the presence of much chloride, no bromide will precipitate under conditions that would cause the precipitation of the whole of it if chlorides were not present.

(best in very small pieces) with a little dilute sulphuric acid. Allow the action to continue until the precipitates have become black (metallic silver), then filter, and collect the filtrates in clean test-tubes. Add to each a little carbon disulphide, then chlorine-water gradually, with shaking.

Under certain conditions, the process of analysis indicated above can be greatly simplified. Supposing that the sulphide and cyanide radicals are absent or have been removed: if a test made with a small portion shows that no iodide is present, another portion of the same solution is tested directly for a bromide, and if this also is absent, any precipitate produced by silver nitrate must be silver chloride.

Where substances insoluble in acids are to be analyzed for the acid radicals of this group, a fusion with sodium carbonate, and treatment of the resulting mass with water, will in all cases bring chlorine, bromine, and iodine into solution as sodium salts. Moreover, the silver salts of the radicals under consideration, and also silver cyanide, are decomposed by treatment with metallic zinc and dilute sulphuric acid. The fusion of a cyanide with sodium carbonate usually destroys the cyanogen. Silver cyanide is characterized by the fact, that upon simple ignition it is decomposed, with the formation of metallic silver.

When a substance contains cyanides, it may happen that certain metals, especially iron and cobalt, may be present in the form of ferrocyanides, ferricyanides, cobalticyanides, etc., under which circumstances these metals fail to give their usual reactions. For example, potassium ferrocyanide, although containing iron, fails to give a precipitate either with ammonium hydroxide or ammonium sulphide. All such cyanides are destroyed by prolonged treatment with boiling concentrated sulphuric acid, and the solution of the residue can be analyzed for the metals in the usual way.*

* For a more comprehensive method for the analysis of cyanides, see Fresenius, p. 529.

A number of sulphides which are insoluble in water are dissolved by hydrochloric or sulphuric acid, with the evolution of hydrogen sulphide. The latter gas is readily detected from the fact that it blackens paper which has been impregnated with an alkaline solution of a lead salt, such as lead acetate solution made strongly alkaline with sodium or potassium hydroxide. All sulphides, except those of mercury, gold, platinum, etc., are decomposed by hot nitric acid, either with separation of all the sulphur in the solid state, or with a more or less extensive formation of sulphuric acid, according to the strength of the acid and the temperature. Aqua regia changes the sulphur of all sulphides, more or less completely, to sulphuric acid. Fusion with oxidizing agents, *e.g.*, a mixture of sodium carbonate and potassium nitrate, changes sulphides to sulphates, and in the case of this mixture, a treatment of the resulting mass with water dissolves the sulphates. It is frequently convenient to convert sulphides into sulphates by one of the preceding or other methods, and detect the sulphur in the latter form.

CHAPTER XII.

GROUP B. (FRESENIUS'S GROUPS I AND III.)

ACID RADICALS WHOSE SILVER SALTS DO NOT FORM PRECIPITATES IN DILUTE ACID SOLUTIONS.

To dilute solutions of salts of each of the acid radicals add barium chloride solution.* In the cases where a precipitate forms add hydrochloric acid to find which precipitates are soluble in acids. Which acid can be detected by this reaction? See if this precipitation takes place when hydrochloric acid is added before adding barium chloride.

This test may be useful in determining the presence or absence of a number of acids (Fresenius's Group I), but it must be remembered that the solution to be tested should be neutral, that it should be concentrated, because some of the barium salts are somewhat soluble in water, and that in some instances, the presence of ammonium salts greatly increases this solubility.

Borates, BO_3''' , BO_2' , $\text{B}_4\text{O}_7''$, *etc.*—Acidify the solution of a borate with hydrochloric acid, dip into the liquid a piece of turmeric-paper, and dry this by placing it upon the outside of a test-tube in which water is being boiled. Dilute solutions should be concentrated by evaporation before this test is

* Potassium cyanide is seldom obtained entirely free from potassium carbonate, because atmospheric carbon dioxide and water displace hydrocyanic acid. A precipitate of barium carbonate is therefore to be expected in the potassium cyanide solution.

made, and they must be made alkaline while being evaporated, because boric acid volatilizes with steam from acid solutions.

Perform the same experiment with turmeric-paper, using dilute sulphuric acid instead of a borate solution. What is the cause of the result? Repeat the experiment, making the sulphuric acid solution alkaline with sodium or potassium hydroxide or carbonate, then acidify with hydrochloric acid, and finally apply the turmeric-paper test.

Perform the same experiment with turmeric-paper, using a borate solution containing a relatively large amount of a chlorate. Mix a dry borate with a dry chlorate, heat to redness in a porcelain crucible until effervescence has nearly ceased, dissolve the residue in a little hydrochloric acid and apply the turmeric-paper test.

Under the conditions of the boric acid test certain substances, such as ferric, zirconium and titanium salts, give changes of color with turmeric-paper. These colors are not identical with that given by borates, but they may lead to uncertainty. These interfering substances may be precipitated by boiling the solution with sodium or potassium hydroxide or carbonate in slight excess, then, after filtering and concentrating, if necessary, the boric acid test may be applied to the solution acidified with hydrochloric acid.

Substances insoluble in hydrochloric acid can be tested for boric acid by fusing with about four parts of sodium carbonate, treating the resulting mass with water, filtering, and treating the liquid as usual.

Carbonates, CO₂.—Treat a solid carbonate and also the solution of a carbonate with dilute hydrochloric acid. Observe the properties of the gas. Mix solutions of a carbonate, a cyanide, and a sulphide in a distilling-bulb which is provided with a cork and a delivery-tube extending into a test-tube containing calcium hydroxide solution. Acidify the contents of the distilling-bulb, quickly insert the cork, and

heat the liquid so that the gases pass over into the calcium hydroxide solution. What is the precipitate formed?

All carbonates effervesce with acids, but in the case of natural magnesium carbonate, the action is very slow, even with hot acid. The acid chosen for the test should be one which does not form an insoluble compound with the metal of the carbonate. Sometimes effervescence does not take place if the acid is too strong. For example, native lead carbonate does not effervesce with nitric acid unless this is considerably diluted, because lead nitrate is insoluble in strong nitric acid, and it is probable that this forms a film on the surface of the substance and protects it.

Chlorates, ClO_3' .—Treat a very *small* amount of a dry chlorate in a dry test-tube with concentrated sulphuric acid, and notice the color and odor. Perform the same operation with a dry iodide, and also with a bromide, in order to find if these interfere with the reaction.

Heat a small amount of a chlorate to redness, dissolve the residue in water, and add nitric acid and silver nitrate solution. Try silver nitrate with the original solution of a chlorate which has not been ignited.

Mix small amounts of solutions of a chlorate and an iodide, acidify slightly with nitric acid, and add silver nitrate solution as long as a precipitate is formed. Filter off the silver iodide, make sure that silver nitrate produces no further precipitation in the filtrate, make it alkaline with sodium carbonate solution (Why?), evaporate to dryness, heat the residue to redness in a porcelain crucible until the mass becomes nearly white, treat with water, filter, and after acidifying the filtrate with nitric acid, test with silver nitrate.

Fluorides, F' .—By the aid of heat, apply a thin coating of paraffin to the concave surface of a small watch-glass (beeswax will not answer the purpose), and, after cooling, trace lines through the paraffin, best with a pointed piece of wood. Place a little finely powdered fluoride, *e.g.*, fluorite or cryolite,

upon the watch-glass, and add a few drops of concentrated sulphuric acid. By means of a strip or roll of paper, spread the mixture over the marked paraffin surface, allow it to stand without heating for five minutes or more. Finally wash off the acid, melt the paraffin and rub it off with paper, and examine the surface of the glass.*

When silicates are present in the substance to be tested, the etching test for fluorides may not succeed, because the fluorine may combine with the silicon of the substance without attacking the silicates of the glass.

Put a dry fluoride mixed with powdered glass into a dry test-tube provided with a rubber stopper with two holes into which two dry glass tubes are fixed. Through one of the tubes, which extends nearly to the bottom of the test-tube, air which has been dried by passing through concentrated sulphuric acid, or otherwise, is passed slowly in. The other tube, extending but little below the stopper, is so bent that it carries the air and the gas that is to be evolved into a very little water contained in another test-tube. Add concentrated sulphuric acid to the mixture, and gradually heat by means of a small flame while passing in a slow current of air.†

Some compounds containing fluorine, especially natural silicates, are not decomposed by sulphuric acid. In such cases the pulverized substance is fused with four or five parts of a mixture of sodium and potassium carbonates. Where the substance does not contain an excess of silica, an equal weight (or less) of pure silica is added before the fusion is made. The mass is soaked out with water, and the solution is filtered. When enough silica has been present so that the bases other

* This convenient modification of the etching test is due to Prof. S. L. Penfield. See Brush and Penfield's "Determinative Mineralogy," p. 75.

† Another method for detecting fluorine in the presence of silica consists in igniting the substance in a bulb-tube, with potassium disulphate or sodium metaphosphate, and noticing the etching and deposit of silica in the tube above the mixture. For the details of this method, see Brush and Penfield's "Determinative Mineralogy," p. 76.

than alkalies have formed silicates (not fluorides), all the fluorine goes into this solution. The solution is nearly, but not quite, neutralized with acetic acid, an excess of calcium chloride solution is added, the resulting precipitate is filtered off, washed, and dried, and then tested for fluorine according to the method described above for use in the presence of silica.

Nitrates, NO_3' .—Mix the cold solution of a nitrate with an equal volume of concentrated sulphuric acid in a test-tube. Cool the mixture well, and, holding the test-tube in an inclined position so that the liquids will not mix, pour in a considerable volume of a concentrated solution of ferrous sulphate, made by saturating cold water with the pulverized salt. With very small amounts of a nitrate, the reaction may not appear until after some time. Slight agitation, to widen the zone of mixture, improves the delicacy of the test.

Perform the same operation with a moderate amount of the solution of a nitrate to which a rather large amount of a chlorate solution has been added.

Mix a little dry nitrate and chlorate together, and heat to redness in a porcelain crucible for a short time. Dissolve the mass in water, and repeat the test for nitric acid. The ignition changes the chlorate to chloride, and although the nitrate may be changed to nitrite at the same time, the latter gives the same reaction as the former with sulphuric acid and ferrous sulphate.

Apply the test for nitrates to solutions of an iodide and a bromide. Will these substances interfere with the test?

Mix solutions of a nitrate and an iodide, acidify a small portion with sulphuric acid, add silver sulphate solution as long as a precipitate forms, and filter. If the filtrate gives no reaction with silver sulphate, apply the test for the nitrate.

All normal nitrates are soluble in water, and the few basic nitrates that do not dissolve in water are dissolved or decomposed by sulphuric acid, so that the test can be applied.

Oxalates, $\text{C}_2\text{O}_4''$.—Acidify the solution of an oxalate with

dilute sulphuric acid, warm to about blood-heat, and gradually add dilute potassium permanganate, KMnO_4 , solution. Identify the gas by performing the operation in a distilling-bulb, and passing it into a calcium hydroxide solution.

Mix solutions of an oxalate and a carbonate, acidify with sulphuric acid, boil, and then add potassium permanganate solution.

Acidify the solution of an oxalate with acetic acid, dilute largely, and add a dilute solution of calcium chloride.

Such substances as ferrous, stannous, and arsenious salts, as well as iodides, and in strong solutions bromides and chlorides, decompose potassium permanganate solution by reducing it, but in none of these cases is there an effervescence, unless chlorine, Cl_2 , is given off from a hot concentrated solution. Hydrogen peroxide, H_2O_2 , also decomposes potassium permanganate in acid solution, giving an effervescence of oxygen. Certain other organic acids, especially formic acid, are decomposed by potassium permanganate solution, with liberation of carbon dioxide, and, therefore, in the presence of organic matter, the additional test by means of calcium chloride in acetic acid solution is advisable.

All oxalates (of the commoner metals) which are insoluble in water are either dissolved or decomposed by sulphuric acid, so that the test with potassium permanganate may be applied to them. They are also decomposed by boiling with sodium carbonate solution, and the resulting liquid, after being filtered, can be acidified with acetic acid and tested with calcium chloride solution, or acidified with sulphuric acid and tested with potassium permanganate.

Phosphates, PO_4''' .—Acidify the solution of a phosphate with nitric acid, add a few drops of this to several cubic centimeters of molybdic acid mixture, and warm to a little above blood-heat. Gradually add more of the phosphate solution, being sure that the molybdic acid mixture is in excess.

Reverse the preceding operation, adding a few drops of the molybdic acid mixture to a comparatively large quantity of the phosphate solution, and observe the relative delicacy of the reaction.

Perform the same operation in the presence of a rather large quantity of hydrochloric acid, using an excess of the molybdic acid mixture, and observe the effect of hydrochloric acid upon the delicacy of the reaction.

Mix the solution of a phosphate with hydrochloric acid, and add also the solution of a silicate. (The latter renders the test unreliable unless the silica is removed, because it sometimes produces a precipitate resembling ammonium phosphomolybdate.) Evaporate the acid solution to dryness, to render silica insoluble, moisten the residue with concentrated nitric acid, and evaporate to dryness again, in order to remove most of the hydrochloric acid. Moisten this residue with nitric acid, warm, dilute a little with water, filter off the silica, and test the liquid for a phosphate.

Test the reaction of an arsenate with the molybdic solution, using a higher temperature than in the case of a phosphate, *i.e.*, heat to boiling. How can arsenic acid be removed from a solution in order that phosphoric acid can be tested for?

Most phosphates are soluble in nitric acid, if not in water, so that the test with molybdic acid mixture can be applied after the removal of any arsenates, silicates, and chlorides. When a substance is not soluble in acids, it is fused with four or five parts of sodium carbonate, the whole of the resulting mass is treated with water and nitric acid, any interfering substances are removed, and the regular test is applied.

Silicates, SiO_4''' , SiO_4'' , *etc.*—Acidify the solution of a silicate with hydrochloric acid (or nitric acid), evaporate to complete dryness in a casserole, moisten the residue with concentrated hydrochloric acid (or nitric acid), warm gently, dilute with water, transfer to a glass vessel, and notice the appearance of the insoluble residue.

Fuse a fragment of a silicate, feldspar for example, in the sodium metaphosphate bead before the blowpipe.

Most silicates are insoluble in water. Many of them are decomposed by acids, either with separation of silica in an insoluble form, or with partial or complete solution of the silica.

Silicates which are not decomposed by acids can be decomposed by fusion, in platinum, in a finely pulverized condition, with four parts or more of sodium carbonate, or, better, a mixture of sodium and potassium carbonates, at a high temperature, until effervescence ceases. The mass is treated with hot water until it has softened, and the liquid containing the residue is acidified, best with hydrochloric acid where that is admissible.

Whether an originally decomposable silicate or the substance after fusion with sodium carbonate has been treated with acid, it is best at the outset to remove the silica by evaporating to dryness, etc., in order to analyze for the metals.

It is evident that a silicate cannot be tested for the alkali metals after fusion with alkaline carbonates. These as well as other metals can be tested for by dissolving the silicate in hydrofluoric acid, in platinum, evaporating with an excess of sulphuric acid to remove the silicon as fluoride and the excess of hydrofluoric acid, and analyzing the resulting substance. There are a few silicates, however, which do not dissolve in hydrofluoric acid.

A good method for testing for alkali metals in insoluble silicates is as follows: Mix the finely pulverized substance with one part of dry ammonium chloride and eight or ten parts of calcium carbonate. Heat the mixture in a covered platinum crucible until the whole mass is at a low red heat, keeping it at that temperature for about half an hour. Treat the mass (which should have sintered together but not fused) with boiling water, and filter the solution. This solution contains calcium chloride, calcium hydroxide, and any alkali

metals in the form of chlorides. Free it from calcium by precipitation with ammonium carbonate, evaporate, drive off ammonium chloride, and test for the alkali metals as usual.

Silicates are sometimes decomposed by evaporation with sulphuric acid until this becomes concentrated, or by fusing with potassium disulphate. Both these operations leave silica insoluble.

Precipitated silica can be identified by the facts that it dissolves (if it has not been ignited) in a strong boiling solution of sodium carbonate, and that it is volatilized by evaporating with hydrofluoric and sulphuric acids together.

The detection of silicic acid in the presence of comparatively large amounts of fluorides is somewhat difficult. It may be stated here that the solution of such mixtures by means of dilute acids produces hydrofluosilicic acid, H_2SiF_6 , an acid which is not included in the present course. See Fresenius, pp. 327 and 655.

Sulphates, $\text{SO}_4^{''}$.—Acidify the solution of a sulphate with hydrochloric acid, dilute with water, and add barium chloride solution.

Add barium chloride solution to some concentrated hydrochloric acid. Observe the result, and then add a large volume of water. What was the precipitate?

Fuse a little dry barium sulphate, or any other sulphate, with dry sodium carbonate before the blowpipe upon charcoal, and place the part of the charcoal in which the mass has been absorbed, with a few drops of water, upon a bright silver coin. This reaction is applicable to insoluble substances, but it does not distinguish sulphates from compounds containing sulphur in any other form.

Substances which are not soluble in hydrochloric acid are conveniently tested for sulphates by fusing with sodium carbonate (best in platinum) soaking out the mass with water, filtering, and testing the resulting solution, after acidifying it with hydrochloric acid, with barium chloride solution.

CHAPTER XIII.

THE ANALYSIS OF SOLIDS.

Preliminary Tests in the Dry Way.—The “blowpipe tests” are usually studied in connection with a course in determinative mineralogy; hence they will not be considered in detail here.* These operations are often very useful in qualitative analysis, and, in the case of simple bodies, they frequently lead at once to a complete knowledge of their nature. In the case of more complex mixtures, conclusions can often be drawn which are of assistance in the subsequent analysis in the wet way. This blowpipe examination may be more or less extensive according to circumstances, but it is advisable, at least, to make a test for silica with the sodium metaphosphate bead, and to test in the closed tube for water, organic matter, and volatile salts.

A careful examination of the physical properties of the substance, such as color, hardness, form, weight, etc., is often very useful, and a lens or, in some cases, a compound microscope may be an assistance in this examination.

The Preparation of Solutions for Analysis.—A preliminary examination of the solubility of a substance to be analyzed should be made by treating small portions of it, in a pulverized condition, with boiling water, hot, dilute, and concentrated hydrochloric acid, nitric acid, and aqua regia, until solution is effected, if possible.

* See Fresenius, pp. 424-434; and Brush and Penfield's “Determinative Mineralogy.”

If a solvent is found, it is applied to an amount of substance sufficient for an analysis for the metals, and great care should be taken that the amount of acid used is no larger than necessary, especially in the case of nitric acid and aqua regia, which interfere with the precipitation by hydrogen sulphide unless greatly diluted. It is often advisable to evaporate off a large part of the acid used in dissolving the substance, but care should be taken that arsenic and mercury, if present, shall not be wholly lost by the volatilization of the chlorides during this operation. Mercuric chloride may be gradually volatilized with the steam, but this is prevented or hindered by the presence of alkaline chlorides, which form double salts with it. Arsenious chloride, AsCl_3 , goes off rapidly, especially when the hydrochloric acid becomes concentrated. By its oxidizing action, nitric acid, when added to a hydrochloric acid solution, hinders the volatilization of arsenious chloride.

If the preliminary examination shows that complete solution is not effected, even with long heating with the various acids, it is often advantageous to know whether or not a partial solution takes place. If this cannot be determined by simple inspection, filtration of the liquids and evaporation to dryness will determine this point except with very volatile substances. It frequently happens that convenient separations can be made by treating a mixture with solvents. For example, a mixture of common salt, marble, and quartz sand could be very simply analyzed by treating with water and examining the solution, then treating with an acid and detecting the calcium carbonate, and finally identifying the quartz by its physical characters and its behavior under examination with the blowpipe. This is much simpler than if an attempt were made to dissolve everything at the outset, and, in addition, an exact knowledge of the nature of the mixture would be obtained.

In dissolving metallic alloys, treatment with nitric acid

leaves all the gold and, in most cases, all the platinum in the metallic state, and it leaves all the tin as well as most of the antimony undissolved in the form of metastannic and metantimonic acids. The latter substances frequently combine with other oxides, especially with arsenic and phosphoric anhydrides, As_2O_5 and P_2O_5 , causing them to remain undissolved at the same time. In such cases, it is sometimes convenient to examine such a residue separately instead of attempting to obtain a complete solution by the use of aqua regia. This examination is conveniently made by dissolving the acids of tin and antimony in yellow ammonium sulphide, and proceeding by obvious methods.

The majority of substances which are insoluble in acids, especially the silicates, are rendered soluble, or at least decomposable, by fusion with about four parts of sodium carbonate or sodium and potassium carbonates. This treatment has been previously mentioned in connection with the detection of a number of the acid radicals in insoluble substances. Certain substances requiring oxidation are decomposed by fusion with four parts of sodium carbonate and one part of potassium nitrate. Insoluble compounds of tin, antimony, and arsenic, especially the former, may be decomposed by fusion in a covered porcelain crucible with several times their weight of a mixture of equal parts of sulphur and sodium carbonate. The mass is treated with water, the solution is filtered if necessary, and the sulphides of the metals mentioned are precipitated by acidifying with sulphuric acid.

Fusion with acid potassium sulphate is a method which is resorted to, especially for the solution of insoluble basic substances, such as corundum, spinel, etc.

For a systematic method for the examination of substances insoluble in acids, see Fresenius, p. 522.

The behavior of substances with solvents often leads to useful conclusions in regard to their composition. For example, if a body is soluble in water, giving a neutral solu-

tion, it is known at once that a great number of compounds cannot be present, including the phosphates, etc., of the alkali-earth metals, the known absence of which may allow the method of analysis to be simplified. As another example, a substance which is soluble in dilute hydrochloric acid cannot contain silver, nor can it contain both barium and the sulphate radical, so that if one of the latter is present the other must be absent. In this connection, the "Table of Solubilities," Fresenius, p. 738, will afford assistance in regard to the solubility of various salts.

CHAPTER XIV.

THE REAGENTS.

Acetic Acid, sp. gr. 1.04, containing about 30 per cent $\text{HC}_2\text{H}_3\text{O}_2$. This acid is used in very dilute solutions in testing for oxalates by means of calcium chloride; for expelling hydrocyanic acid from boiling solutions; and, with potassium nitrite, for precipitating potassium cobaltic nitrite, thus effecting the separation of cobalt and nickel.

Ammonium Carbonate, $(\text{NH}_4)_2\text{CO}_3$, the "sesquicarbonate" in 4 parts of water and 1 part of ammonium hydroxide solution. It should leave no residue upon evaporation to dryness. This is used as a group reagent, in the presence of ammonium chloride and ammonium hydroxide, for barium, strontium, and calcium; also to precipitate strontium and calcium carbonates in the course of the analysis of this group.

Ammonium Chloride, NH_4Cl , in 10 parts of water. This should leave no residue upon evaporation to dryness and heating to low redness. It is used to prevent the precipitation of manganese hydroxide and magnesium hydroxide when aluminium, ferric, and chromium hydroxides are precipitated as a group with ammonium hydroxide; to prevent the precipitation of magnesium hydroxide when cobalt, nickel, zinc, and manganese sulphides are precipitated as a group with ammonium sulphide; and also to prevent the precipitation of magnesium carbonate when barium, strontium, and calcium

carbonates are precipitated as a group with ammonium carbonate.

Ammonium Hydroxide, NH_4OH , sp. gr. 0.94. This solution, containing about 15 per cent of ammonia, NH_3 , is made by diluting the concentrated liquid with an equal volume of water. It should give no residue upon evaporation to dryness. It is used to precipitate bismuth hydroxide, while cadmium and copper remain in solution, the latter giving a blue color; to neutralize solutions of arsenic acid in nitric acid, containing silver nitrate, in order to precipitate silver arsenate, thus effecting a test for arsenic; in the presence of ammonium chloride to precipitate aluminium, chromium, and ferric hydroxides as a group; as a final test for aluminium; to dissolve silver chloride, in order to separate it from mercurous chloride, the latter forming a black compound; to decrease the solubility of barium, strontium, and calcium carbonates when they are precipitated by means of ammonium carbonate; to the extent of one third of the solution when ammonium magnesium phosphate is precipitated by means of hydrogen sodium phosphate; and also, mixed with 3 volumes of ammonium nitrate solution, to dissolve silver chloride and bromide, in order to separate them from silver iodide.

Ammonium Oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in 24 parts of water. This is used as a final test for calcium; and as a test for a trace of calcium which may have been left in solution after the precipitation by ammonium carbonate.

Ammonium Sulphide, $(\text{NH}_4)_2\text{S}$, is made by saturating NH_4OH solution with H_2S , then adding the same quantity of NH_4OH solution. For laboratory use, this liquid may be diluted with an equal volume of water. The *yellow* solution, $(\text{NH}_4)_2\text{S}_{1+x}$, is formed by the oxidizing action of the air on the colorless solution, or it may be prepared from the latter by dissolving a little sulphur in it. It is used in the presence of ammonium chloride to precipitate cobalt, nickel, zinc, and manganese sulphides as a group; as a final test for zinc in

sodium or potassium hydroxide solution; and especially, the yellow solution to dissolve the sulphides of tin, antimony, and arsenic as a group.

Ammonium Thiocyanate, NH_4CNS , in 10 parts of water. This is used as a test for ferric salts.

Amyl Alcohol, $\text{C}_5\text{H}_{11}\text{OH}$, boiling point about 131° . This is used to separate calcium nitrate from strontium nitrate, since, when it is boiled until it becomes anhydrous, it dissolves the former, but does not dissolve the latter. In the same manner, it is used to separate lithium chloride from sodium and potassium chlorides, as the anhydrous liquid dissolves the former but does not dissolve the last two.

Aqua Regia, HCl and HNO_3 . This is usually made by mixing, immediately before using, about 3 volumes of hydrochloric acid and 1 volume of nitric acid. It is used for dissolving the black product produced by the action of ammonium hydroxide upon mercurous chloride, in order that any silver chloride contained in it may be subsequently detected. It is also used for dissolving mercuric sulphide, or the white compound of mercuric sulphide and nitrate, in order that the presence of mercury may be confirmed; for converting ferrous salts into ferric salts, nitric acid being added to the solution containing hydrochloric acid, before precipitating Group D with ammonium hydroxide; and for dissolving nickel and cobalt sulphides, in order that the two metallic radicals may be subsequently separated.

Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, in 10 parts of water. This is used to convert potassium, sodium, and lithium sulphates into chlorides; as a test for sulphates in acid solutions; in neutral, or in some cases alkaline, solutions, as a test for arsenates, borates, carbonates, chromates, fluorides, oxalates, phosphates, silicates, and sulphates as a group.

Barium Hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, in 20 parts of water. This solution is used, in the absence of ammonium salts, to precipitate magnesium hydroxide; to precipitate barium phos-

phate, borate, etc., in order to separate the acid radicals of these salts from potassium, sodium, and lithium.

Cadmium Sulphate, $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, in 20 parts of water, is used as a test for the sulphide radical, and to remove it from solutions.

Calcium Chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, in 10 parts of water, is used as a test for oxalates in very dilute solutions made slightly acid with acetic acid.

Calcium Hydroxide, $\text{Ca}(\text{OH})_2$. The dry substance is used in testing for ammonium. The saturated solution in water (about 1 part in 700) is used to test for gaseous carbon dioxide.

Carbon Disulphide, CS_2 , is used as a solvent for free iodine or bromine, which impart to it characteristic colors.

Chlorine-water, saturated solution in water (contains about 2 volumes of gas or 0.6 per cent by weight at ordinary temperature). This is used to liberate bromine from bromides in acid solutions.

Ethyl Alcohol, $\text{C}_2\text{H}_5\text{OH}$. Alcohol of 95 per cent will answer. A few drops are occasionally added to the boiling solution where the test for chromium is to be observed, to destroy any pink color of permanganic acid.

Ferric Chloride, $\text{FeCl}_3 \cdot ?\text{H}_2\text{O}$, in 10 parts of water, is used in separating the phosphate radical, etc., from barium, strontium, calcium, and magnesium; also in the test for cyanogen.

Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. A saturated solution in cold water (in about 1 part of water) is used in testing for nitric acid; and a more dilute solution, in the test for cyanogen.

Hydrochloric Acid, HCl . The solution used for most purposes contains somewhat more than 20 per cent of HCl . It is made by diluting the concentrated solution with an equal volume of water. It is used very generally in dissolving substances and acidifying solutions; in precipitating mercurous, silver, and lead chlorides as a group; in precipitating stannic, antimonic, and arsenic sulphides as a group from the solution of the thio-salts; in dissolving the sulphides of tin

and antimony at the boiling temperature, thus separating them from the sulphides of arsenic; in dissolving metallic tin, thus forming stannous chloride and separating it from metallic antimony; when diluted with 3 volumes of water or hydrogen sulphide water, in dissolving zinc and manganese sulphides, thus separating them from cobalt and nickel sulphides; for dissolving barium, strontium, and calcium carbonates, in order to obtain the chlorides.

Hydrochloroplatinic Acid, H_2PtCl_6 , $\frac{1}{20}$ g Pt in 1 cc. This is made by dissolving platinum in aqua regia, evaporating to small bulk on the steam-bath, adding a large excess of hydrochloric acid and evaporating to small volume repeatedly to remove nitric acid, dissolving the residue in water, and diluting to the proper strength. It is used to test for potassium salts in very concentrated solutions.

Hydrogen Sulphide Gas, H_2S , is made from ferrous sulphide and hydrochloric acid in Kipp's (Fresenius, p. 289) or some other form of generator. It is used to precipitate the sulphides of mercury, lead, bismuth, copper, cadmium, tin, antimony, and arsenic in acid solutions. In acid solutions, it reduces ferric to ferrous salts, chromic acid to chromium salts, and permanganic acid to manganese salts.

Hydrogen Sulphide Water, saturated solution of H_2S in water (contains about 3 volumes of the gas at ordinary temperature). It is used for the same purposes as the gas, and especially for testing filtrates from precipitates produced by the gas.

Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, in 10 parts of water, is used in moistening filter-paper for the purpose of testing for the hydrogen sulphide escaping when the sulphides of tin and antimony are dissolved in boiling hydrochloric acid.

Litmus-paper, blue and red. (See Fresenius, pp. 115 and 116.) This is used to test for acids and alkalies in solutions.

Mercuric Chloride, HgCl_2 , in 20 parts of water, is used in testing for stannous chloride as a final test for tin.

Molybdic Acid Mixture, MoO_3 and NH_4NO_3 in dilute HNO_3 . The solution contains about 5 per cent of MoO_3 . (For preparation, see Fresenius, p. 97). It is used in excess in testing for phosphates in warm nitric acid solutions; similarly for arsenates in boiling solutions.

Nitric Acid, HNO_3 . The ordinary solution, containing about 40 per cent of HNO_3 , is made by diluting the concentrated acid (sp. gr. 1.42) with an equal volume of water. It is used for acidifying solutions before precipitating the chlorides of group A with hydrochloric acid; for acidifying the ammoniacal solution of silver chloride in the final test for silver; when diluted with about an equal volume of water and boiling, to dissolve lead, bismuth, copper, and cadmium sulphides, thus separating them from mercuric sulphide; for dissolving the sulphides of arsenic, thus producing arsenic acid; for dissolving, with the aid of tartaric acid, coatings of metallic antimony on the platinum foil; for oxidizing ferrous salts in boiling solutions, usually in the presence of hydrochloric acid, thus converting them into ferric salts; for dissolving strontium and calcium carbonates, thus producing the nitrates; for acidifying solutions before adding silver nitrate in precipitating silver chloride, bromide, iodide, etc.; for acidifying the ammoniacal solutions of silver bromide and chloride, in order to precipitate the latter compounds; for acidifying solutions, or, with the aid of evaporation, for removing hydrochloric acid and silica, before testing for phosphates with molybdic acid solution.

Potassium Chlorate, KClO_3 . The dry salt is used as an oxidizing agent, with sodium carbonate, in testing for manganese by fusion.

Potassium Cyanide, KCN . This is preserved in the solid state, since the solution does not keep well. It is used in solution for dissolving cupric sulphide, thus separating it from cadmium sulphide.

Potassium Dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, in 10 parts of water.

It should not contain potassium sulphate. The solution is used in testing for barium, and separating it from strontium and calcium, by precipitating barium chromate from neutral solutions containing sodium acetate; for liberating iodine from acid solutions of iodides.

Potassium Ferricyanide, $K_3Fe(CN)_6$. This is kept as a solid, since the solution gradually decomposes. It is used in the form of a freshly prepared, dilute solution in testing for ferrous salts.

Potassium Ferrocyanide, $K_4Fe(CN)_6$, in 20 parts of water, is used in testing for ferric salts.

Potassium Hydroxide, KOH , in 10 parts of water, is used for the same purposes as sodium hydroxide.

Potassium Nitrite, KNO_2 . The solid is used to precipitate cobalt in the form of potassium cobaltic nitrite, from very concentrated solutions acidified with acetic acid, thus separating cobalt from nickel.

Potassium Permanganate, $KMnO_4$, in 20 parts of water, is used for detecting oxalic acid in warm, acid solutions.

Potassium Sulphate, K_2SO_4 , in 12 parts of water, is used in testing for strontium (when no barium and very little calcium can be present).

Silver Nitrate, $AgNO_3$, in 20 parts of water. This is used to detect arsenic acid in neutral solutions; in the presence of nitric acid to test for sulphides, cyanides, iodides, bromides, and chlorides as a group, to precipitate silver chloride, bromide, and iodide, in order that the first two may be separated from the last by treatment with the ammoniacal solution of ammonium nitrate; to precipitate silver bromide from its solution in ammoniacal ammonium nitrate, thus allowing silver chloride, if present, to be detected; to remove the chloride, bromide, and iodide radicals from solutions to be tested for chlorates, so that the latter may be converted into chlorides by ignition and thus detected.

Silver Sulphate, Ag_2SO_4 , saturated solution in water

(dissolves in about 200 parts of cold water. A stronger solution—of HAgSO_4 —may be made by using dilute sulphuric acid). It is used for removing the iodide and bromide radicals from solutions to be tested for nitrates.

Sodium Acetate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, in 10 parts of water. This is used in precipitating ferric, aluminium, and chromium basic acetates, and, under certain circumstances, their phosphates, oxalates, etc., in very dilute, nearly neutral solutions at the boiling temperature; in connection with potassium dichromate, for completely precipitating barium chromate from neutral solutions.

Sodium Carbonate, Na_2CO_3 . Solid. This is used in a fused condition at a red heat for decomposing many substances insoluble in acids; when fused with an oxidizing agent, such as potassium chlorate or nitrate, or even in the presence of atmospheric oxygen, as a test for manganese.

Sodium Carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, in $2\frac{1}{2}$ parts of water, is used for neutralizing acids.

Sodium Hydroxide, NaOH , in 10 parts of water. No precipitate should be produced when the solution is acidified with hydrochloric acid, ammonium hydroxide then added in slight excess, and the liquid is boiled. It is used with stannous chloride to prepare sodium stannite solution for use in testing for bismuth; at the boiling temperature, to dissolve aluminium hydroxide, thus separating it from chromium and ferric hydroxides, and cold, to dissolve zinc hydroxide, thus separating it from manganese hydroxide.

Sodium Hypochlorite, NaClO , a solution containing sodium hydroxide and sodium chloride, is made by saturating cold sodium hydroxide solution with chlorine gas and adding an equal volume of the sodium hydroxide solution. It is used at the boiling temperature to dissolve chromium hydroxide, thus producing sodium chromate, and furnishing a test for chromium.

Sodium Phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, in 10 parts of water,

is used in the presence of one third of the final volume of ammonium hydroxide as the test for magnesium.

Sodium Sulphide, Na_2S , is made by saturating sodium hydroxide solution with hydrogen sulphide gas, and adding the same volume of sodium hydroxide solution. It is used occasionally to dissolve the sulphides of tin, antimony, and arsenic, in order to separate from them a minute quantity of cupric sulphide, which frequently dissolves in ammonium sulphide, and is precipitated by hydrochloric acid along with the sulphides in question.

Sodium Tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Solid. This is used as a blowpipe bead (after driving off the water of crystallization) in testing for cobalt and nickel.

Stannous Chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, in 10 parts of water, acidified with hydrochloric acid. To prepare the solution from metallic tin, see Fresenius, p. 112. It is used in testing in acid solutions for mercuric salts. When stannous chloride solution is made alkaline, and the resulting precipitate dissolved by sodium hydroxide, sodium stannite results, which is used in testing bismuth hydroxide precipitates.

Sulphuric Acid, H_2SO_4 . The concentrated acid contains about 98 per cent of the pure substance. The dilute acid is made by mixing 3 volumes of water with the concentrated acid, and contains about 37 per cent of H_2SO_4 . The dilute acid is used in testing the solution of lead chloride in hot water; by means of evaporation, to convert the nitrates of lead, bismuth, copper, and cadmium into sulphates, all of which except lead sulphate dissolve in water containing dilute sulphuric acid; at the boiling temperature, to dissolve cadmium sulphide, thus separating it from traces of black sulphides; after neutralization with ammonium hydroxide and the formation of ammonium sulphate, for the detection and removal of traces of barium which may have escaped precipitation with ammonium carbonate; for acidifying solutions to be tested for iodides, where potassium dichromate

and carbon disulphide are added; with metallic zinc in reducing silver bromide and chloride, in order that bromine may afterwards be detected by the use of chlorine-water and carbon disulphide. The concentrated acid is used in detecting chlorates; in the test for nitric acid; and in testing for fluorides.

Tartaric Acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Solid. A little of this acid is occasionally used with nitric acid in dissolving the coatings of metallic antimony from the platinum foil.

Zinc, Zn. Metallic. This is used in small pieces in contact with platinum foil, for precipitating metallic tin and antimony from solutions containing stannic and antimonious chlorides and hydrochloric acid; in the presence of sulphuric acid, for reducing silver bromide and chloride, in order that bromine may afterwards be detected by means of chlorine-water and carbon disulphide.

PART II.

THEORY.

CHAPTER XV.

CHEMICAL RADICALS AND FORMULAS.

WHEN the *valence* of the various atoms and groups of atoms is known, it becomes a simple matter to write the formulas of the ordinary chemical compounds, especially those of the inorganic acids, hydroxides (bases), and salts, which are encountered in the study of analytical chemistry.

The atoms and groups which readily change places with each other in solution (*i.e.*, those which take part in simple chemical reactions), as far as the commoner elements and inorganic compounds are concerned, are given in the table which follows. They are classified as positive and negative atoms or groups, which may be called radicals. As a rule, any radical may form compounds with all or nearly all the opposite kind of radicals, but there are a few cases where the number of compounds is more or less limited. The valence is indicated by dots in the case of positive radicals, and by accent marks in that of negative radicals. Nearly all these radicals act as ions, which will be discussed subsequently.

POSITIVE (METALLIC)
RADICALS.

Univalent (Valence 1).

NH_4^+ , Ammonium
Cu^+ , Cuprous
H^+ , Hydrogen
Li^+ , Lithium
Hg^+ , Mercurous
K^+ , Potassium
Ag^+ , Silver
Na^+ , Sodium

Bivalent (Valence 2).

Ba^{++} , Barium
Cd^{++} , Cadmium
Ca^{++} , Calcium
Co^{++} , Cobalt
Cu^{++} , Cupric
Fe^{++} , Ferrous
Pb^{++} , Lead
Hg^{++} , Mercuric
Mg^{++} , Magnesium
Mn^{++} , Manganese
Ni^{++} , Nickel
Sn^{++} , Stannous
Sr^{++} , Strontium
Zn^{++} , Zinc

Trivalent (Valence 3).

Al^{+++} , Aluminium
Sb^{+++} , Antimonious
Bi^{+++} , Bismuth
Cr^{+++} , Chromium
Fe^{+++} , Ferric

Quadrivalent (Valence 4).

Sn^{++++} , Stannic

NEGATIVE (ACID)
RADICALS.

Univalent (Valence 1)

$\text{C}_2\text{H}_3\text{O}_2^-$, Acetate
Br^- , Bromide
ClO_2^- , Chlorate
Cl^- , Chloride
CN^- , Cyanide
F^- , Fluoride
OH^- , Hydroxide
ClO^- , Hypochlorite
I^- , Iodide

NO_3^- , Nitrate
NO_2^- , Nitrite
MnO_4^- , Permanganate
CNS^- , Thiocyanate

Bivalent (Valence 2).

CO_3^{--} , Carbonate
PtCl_6^{--} , Chloroplatinate
CrO_4^{--} , Chromate
$\text{Cr}_2\text{O}_7^{--}$, Dichromate
MnO_4^{--} , Manganate
SiO_3^{--} , Metasilicate
O^{--} , Oxide
SO_4^{--} , Sulphate
S^{--} , Sulphide
SO_3^{--} , Sulphite
SnS_3^{--} , Thiostannate

Trivalent (Valence 3).

AsO_4^{--} , Arsenate
BO_3^{--} , Borate
$\text{Fe}(\text{CN})_6^{--}$, Ferricyanide

PO_4^{--} , Phosphate
SbS_4^{--} , Thioantimonate

POSITIVE (METALLIC) RADICALS.	NEGATIVE (ACID) RADICALS.
<i>Quinquivalent (Valence 5).</i> Sb $\cdots\cdots$, Antimonic *	AsS $_4$ $'''$, Thioarsenate
As $\cdots\cdots$, Arsenic *	<i>Quadrivalent (Valence 4).</i> Fe(CN) $_6$ $'''$, Ferrocyanide
	SiO $_4$ $'''$, Orthosilicate

The following rules may be of assistance in writing the formulas of compounds:

1. *Radicals having the same valence combine one to one, e.g., NaBr, BaSO $_4$, AlPO $_4$, etc.*
2. *Radicals having different valences are to be taken each as many times as the valence of the other, e.g., K $_2$ SO $_4$, CdCl $_2$, Al(NO $_3$) $_3$, Ag $_3$ PO $_4$, Ba $_3$ (PO $_4$) $_2$, Bi $_2$ (SO $_4$) $_3$, SnS $_2$, † Fe $_4$ [Fe(CN) $_6$] $_3$, etc.*

The names of the simple compounds are formed from the names of the radicals which have been given in the table, but hydrogen hydroxide and hydrogen oxide are, of course, the same thing as water. The other hydrogen compounds may be called hydrogen chloride, hydrogen nitrate, hydrogen sulphate, etc., but, especially when in aqueous solution, they usually receive the older designation, being called acids, *e.g.*, hydrochloric, nitric, sulphuric acid, etc.

There are cases where two or three *different* positive radicals combine with a negative radical, or where *more than one* kind of negative radicals combine with a positive one. In these cases, the sum of the valences of the radicals of the same sign is equal to the valence of the radical with which they combine; thus, HKSO $_4$, hydrogen potassium sulphate; HNaCO $_3$, hydrogen sodium carbonate; HNa $_2$ PO $_4$, hydrogen disodium phosphate; HNH $_4$ NaPO $_4$, hydrogen ammonium

* Sb $\cdots\cdots$ and As $\cdots\cdots$ form SbCl $_5$, Sb $_2$ O $_5$, Sb $_2$ S $_5$, As $_2$ O $_5$, and As $_2$ S $_5$, but do not combine with most of the negative radicals given above.

† The resulting formula is simplified by division by 2 where a bivalent and quadrivalent radical are united by this rule.

sodium phosphate ; $\text{NH}_4\text{MgAsO}_4$, ammonium magnesium arsenate ; $\text{KAl}(\text{SO}_4)_2$, potassium aluminium sulphate ; BiOCl , bismuth oxychloride ; $\text{Pb}(\text{OH})\text{Cl}$, lead hydroxychloride. Such of these compounds as contain positive hydrogen are called *acid salts*, while those containing negative hydroxyl or oxygen are called *basic salts*. Those compounds which may be regarded as being composed of two separate salts, *e.g.*, $\text{KAl}(\text{SO}_4)_2$, which may be written $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$, are called *double salts*. It is evident that the acid salts may be also regarded as double or triple salts.

CHAPTER XVI.

IONIZATION AND IONS.

ACIDS, hydroxides, and salts, as far as they are soluble in water, with few exceptions,* show a peculiar behavior when they are dissolved in the liquid just mentioned. Unlike many other chemical compounds, they readily undergo reactions when in solution, *i.e.*, they easily exchange radicals with each other. In nearly all cases, the radicals which have been given in the preceding chapter, in the list of positive and negative radicals are readily capable of changing places with others.

There can be no doubt that acids, bases, and salts readily exchange their radicals in solution, for it is an established fact that it makes absolutely no difference in what state of combination the radicals present in a solution have been introduced. For example, if an equal number of molecules of sodium chloride and potassium nitrate are dissolved in water, the solution is *identical* in all its properties with a solution prepared with the same number of molecules of potassium chloride and sodium nitrate and the same amount of water. In the same way, identical solutions may be made with ammonium sulphate and hydrochloric acid and with ammonium chloride and sulphuric acid; or, in fact, any two mixtures of salts, acids, and hydroxides, will give identical solutions, provided that the various radicals are present in the same proportions.

* Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is an example of a salt which is an exception in some respects.

Since the compounds under consideration are capable of exchanging radicals, while other exchanges involving the constituents of the compound radicals do not take place,* it must be admitted that these positive and negative radicals *separate from each other* in some way when the compounds are dissolved. This separation is called *ionization*, and the separated radicals are called *ions*.

These radicals or ions are set free† in equivalent numbers at the negative and positive electrodes when an electric current is passed through a solution of a salt, acid, or hydroxide. In fact, it is only solutions of these compounds that conduct electricity, and the compounds are therefore called electrolytes.

It is believed that the electrical conductivity of a solution depends upon the extent of ionization of the dissolved substance, *i.e.*, upon the proportion of the molecules which at any one time are separated into their ions. It has been possible, therefore, to study the behavior of many compounds in this respect. It has thus been found that ionization varies greatly with different salts, but that, in all cases, its extent increases with the dilution, so that at infinite dilution, ionization must be complete.

The idea of an ion must be kept entirely distinct from that of a molecule. Ions cannot exist except in solution. One kind of ions cannot exist alone, for the positive ions in a solution are always exactly counterbalanced by an equivalent number of negative ions (one bivalent ion being equivalent to two univalent ions, etc.). The positive and negative ions

* For instance, the sulphur atom of the sulphate radical is unable to form a sulphide by simple exchange, the chlorine atom of the chlorate radical behaves in a similar manner, etc.

† When set free, an ion may assume the molecular condition and be deposited as a metal or escape as a gas, or it may combine with the substance composing the electrode, or it may at once effect the decomposition of the water present, causing the formation of hydrogen at the negative pole or of oxygen at the opposite pole.

in a solution, although they are free to move to a certain extent, hold each other under control, for no separation (beyond mutual control) of positive from negative ions takes place by diffusion through a porous diaphragm (as is the case with lighter and heavier molecules). It seems probable that ions owe their behavior to charges of positive and negative electricity. When this electricity is discharged by the passage of an electric current, the atom or group composing the ion assumes the chemical properties that would be expected of it in an entirely free condition. For instance, the ions of sodium sulphate, 2Na^+ and SO_4^{--} , do not decompose water when in the ionic condition and in presence of each other, but they do have such an action when their electricity has been discharged, and they are removed from mutual control.

It is an interesting fact that the most powerful acids and hydroxides are those which are most extensively ionized in solution, and, therefore, that chemical activity depends upon ionization. As an example of this, hydrochloric acid, which is readily ionized in solution, is a powerful solvent for many substances, while acetic acid, which is ionized to a much smaller extent, has, in most cases, a much less energetic action on account of the smaller number of hydrogen ions which it liberates. If sodium acetate is added in excess to a solution of hydrochloric acid, the hydrogen ions attach themselves to the acetate ions, and being no longer free to move except to a very limited extent, the resulting solution has practically the solvent action of an acetic acid solution. Of course, the solution just mentioned could be exactly duplicated by the use of the proper amounts of acetic acid, sodium chloride, and sodium acetate, and hence the old explanation of the result was that the stronger acid set free the weaker one from its salt. This is practically true, but the old method does not explain why hydrochloric is stronger than acetic acid.

A full discussion of ionization will not be attempted here,

but the important fact may be mentioned that substances, the molecules of which are not ionized, exert in solution an osmotic pressure which corresponds to the pressure they would be expected to give in the gaseous condition at the same temperature and occupying the same volume; while compounds which are ionized exert a greater pressure than that which is calculated according to the laws of gases.* This fact indicates that some of the molecules of the latter class of compounds are divided when in solution, and it is a strong argument in favor of the ionic theory.

The circumstance that ionization takes place greatly simplifies inorganic chemical analysis. It is merely necessary to detect the ions that a solution contains, without regard to the multitude of combinations that they may form. Thus, silver is easily detected in a solution on account of the behavior of its ion, and this behavior is the same for all soluble silver salts. Again, it is not necessary to make a separate test for every soluble chloride, for the chloride ion is readily detected, whatever the dissolved salt may be (provided that the salt becomes ionized).

* Experiments with osmotic pressure have been made by the use of diaphragms which permit water to pass through them, but which do not allow the dissolved substance to pass, *e.g.*, a small, unglazed porcelain cell, in the pores of which cupric ferrocyanide has been precipitated. If such a cell is filled with the solution of some substance, connected water-tight with a long, upright glass tube (or a manometer), and dipped into water, the latter will enter the cell more rapidly than it passes out, on account of the osmotic pressure of the dissolved substance, and the liquid will rise in the tube until equilibrium is established. Pressures obtained in this way are often very great, amounting to many atmospheres.

CHAPTER XVII.

PRECIPITATION.

THERE is a direct connection between the formation of precipitates and insolubility. A compound which is readily soluble in the liquid that is present *cannot* form a precipitate in the presence of a sufficient amount of that liquid.

When two or more solutions are mixed, if positive and negative ions are present which by their union form a compound insoluble in the resulting liquid, these ions will unite in equivalent numbers, and the insoluble compound will separate in the solid state. This process will go on rapidly until one or the other of the ions is completely removed from the solution, or both of them are removed if they were present in equivalent numbers. For example, if solutions of a silver salt and a chloride are mixed, a precipitate of silver chloride will result if the solution is neutral or acid. If the chloride is in excess, no silver salt will remain in the solution, while no chloride will remain if the silver salt is in excess. If the silver and chlorine atoms are present in equal numbers, both will be removed from the solution. The chlorine atom of a chlorate will not form silver chloride by exchange in solution, because, in this case, the atom does not form an ion, the chlorate ion being ClO_3' . For the same reason, the ferrous atom of a ferrocyanide gives none of the reactions of the ferrous ion.

A salt which is slightly soluble in the liquid present may form a precipitate, but, in this case, enough of the salt to

saturate the solution must remain dissolved. The removal of either ion cannot be complete under these circumstances. For instance, lead chloride forms a precipitate when moderately concentrated solutions of a lead salt and a chloride are mixed, but if either of the solutions is very dilute, no lead chloride will precipitate, because the amount of water present is sufficient to dissolve all that can be formed. In any case, neither lead nor chlorine can be completely removed by this precipitation, because the water present must dissolve some lead chloride.

An inspection of the "Table of Solubilities" (Fresenius, p. 738) will show what compounds are soluble in water (*W* or *w*), and which, consequently, cannot form precipitates when an exchange of radicals may produce them. Those salts which dissolve in acids, but not in water (*A* or *a*), may be expected to precipitate in neutral and possibly in alkaline solutions, while those insoluble in acids (*I* or *i*) may form precipitates in neutral and acid solutions, and possibly also in alkaline solutions. For example, all the normal acetates, nitrates, and chlorates are soluble in water, hence these salts do not form precipitates; mercurous and silver chlorides, and to a less degree, lead chloride, are insoluble in acids, hence they may be expected to form precipitates in neutral and acid solutions. A similar examination will show that barium, strontium, calcium, and lead sulphates are the only common sulphates that form precipitates in moderately dilute solutions.

CHAPTER XVIII.

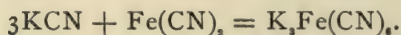
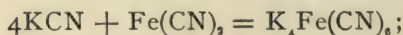
CRYSTALLIZATION FROM MIXED SOLUTIONS.

THE term crystallization is applied to the comparatively slow separation, in the crystalline form, of relatively soluble substances. In mixed solutions there is no dividing line between precipitation and crystallization, and the least soluble salt formed by ionization is first deposited when the solvent is saturated with it, upon proper concentration or cooling, or by the use of both means. For example, if a solution is prepared either from sodium chloride and potassium nitrate or from sodium nitrate and potassium chloride, it will contain the four ions and all the combinations of them, *viz.*, Na^+ , K^+ , Cl^- , NO_3^- , NaCl , KCl , NaNO_3 , and KNO_3 . Upon evaporating this solution, it will become saturated with one of these salts, and this will crystallize first; then, when the liquid becomes saturated with another salt, formed from the radicals remaining in solution, two salts will be deposited together, and, by continuing the evaporation, it is possible that a mixture of three, and finally one of four salts may be obtained.

The products resulting from the crystallization of solutions of certain mixtures of salts frequently include double salts, *i.e.*, combinations of two simple salts in one or more proportions. Some of these double salts require the presence in solution of an excess of one or the other of their constituent salts, in order that they may be formed, while others do not. Thus, if a solution containing an equal number of molecules of potassium chloride, KCl , and magnesium chloride, MgCl_2 ,

is evaporated, potassium chloride alone will first crystallize out, upon cooling the sufficiently concentrated solution; then, upon further evaporation, when the solution contains a sufficient excess of magnesium chloride, the double salt, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, will be deposited, and at last the excess of the very soluble magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, may be crystallized, mixed with some of the double salt which has still remained in solution. On the other hand, if an equal number of molecules of potassium sulphate, K_2SO_4 , and aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, are dissolved in water, nothing but alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, can be crystallized from the solution, because this double salt does not require the presence of an excess of either of its constituents for its formation.

The stability of double salts with respect to water varies greatly, some of them recrystallizing unchanged from water (*e.g.*, alum), others requiring special conditions for their formation. Many double salts are evidently decomposed by solution in water, for their solutions give the reactions for all the ions of the constituent salts, but there is a class of double compounds which are not decomposed by water in this way. For example, potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, and potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, are formed by the union of ferrous and ferric cyanides with potassium cyanide. Thus,



The solutions of these compounds do not give reactions for Fe^{++} , Fe^{+++} , or CN' , but, while each of them gives the reactions for K^+ , one furnishes the ion $\text{Fe}(\text{CN})_6^{++++}$, and the other $\text{Fe}(\text{CN})_6^{+++}$.

CHAPTER XIX.

THE FORMATION OF VOLATILE COMPOUNDS.

IONIZATION, in many cases, leads to the production of volatile compounds. Thus, if a solution of a chloride is mixed with sulphuric acid (hydrogen sulphate), the movement of the ions permits the formation of hydrochloric acid (hydrogen chloride), and if the solution is evaporated, the latter compound escapes with the water-vapor when the solution becomes sufficiently concentrated, while sulphuric acid, being much less volatile, cannot evaporate till practically all the water has been driven off. An excess of sulphuric acid, therefore, will completely change a soluble chloride into a sulphate upon evaporation; whereas a sulphate cannot be converted into a chloride by means of evaporation with hydrochloric acid. This behavior of the less volatile acid is general, except in cases where the latter is but slightly ionized (*i.e.*, it is a weak acid, as are most of the organic acids). In this case, the weak acid liberates comparatively few hydrogen ions, so that there can be formed only a small quantity of the more volatile but stronger acid whose negative ion separates from the hydrogen ion more readily. Thus, the quantity of the stronger acid may be so small that none of it can volatilize with the water-vapor,* even upon evaporation to dryness, for equilibrium is maintained by ionization as the evaporation proceeds.

* Very dilute aqueous solutions of many volatile acids, such as hydrochloric and nitric acids, lose nothing but water upon evaporation, until a certain degree of concentration has been reached.

CHAPTER XX.

THE CLASSIFICATION OF RADICALS AND SALTS.

AN inspection of the list of radicals which has been previously given shows that most of the positive radicals considered consist of a single atom, while many of the negative radicals consist of groups, usually of atoms of two elements. The radicals are therefore atomic or compound.

Hydrogen occurs in the radicals $H\cdot$, $NH_4\cdot$, $OH\cdot$, $C_2H_5O_2\cdot$, and in a vast number of other groups not considered here, which are chiefly the radicals of organic bases and acids.* The hydrogen atom is supposed to be univalent in all positions.

Oxygen occurs in a large number of the compound negative radicals. When combined with positive radicals, these form the oxygen salts and acids.

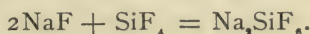
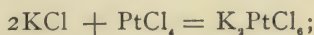
There are several radicals, to the names of which the

* In this connection, the fact should be mentioned that the hydrogen ion $H\cdot$ is not as readily liberated as many other positive radicals, so that in the ionization of acid salts (which have already been alluded to) one or more hydrogen atoms practically form a part of the negative ion. Thus, $KHSO_4$, potassium hydrogen sulphate, is ionized chiefly into $K\cdot$ and $HSO_4\cdot$; the salt Na_2HPO_4 , disodium hydrogen phosphate, forms chiefly $2Na\cdot$ and $HPO_4\cdot$; while NaH_2PO_4 , sodium dihydrogen phosphate, gives principally the ions $Na\cdot$ and $H_2PO_4\cdot$. It may be added that where two or more positive radicals of the same kind are combined with a negative radical, one of the former is apparently more readily ionized than the other or others, so that the ionization of a salt like Na_2SO_4 may form the ions $Na\cdot$ and $NaSO_4\cdot$ to a certain extent, and H_3PO_4 gives chiefly $H\cdot$ and $H_2PO_4\cdot$.

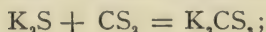
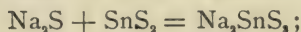
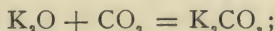
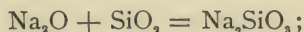
prefix "thio" is applied, which form thio, or sulphur, salts and acids, in which sulphur takes the place of the oxygen in oxygen salts. Thus, the following radicals correspond to each other:

CNO', cyanate,	and	CNS', thiocyanate;
SnO ₃ '', stannate,	and	SnS ₃ '', thioannate;
CO ₃ '', carbonate,	and	CS ₃ '', thiocarbonate;
AsO ₄ '', arsenate,	and	AsS ₄ '', thioarsenate.

The salts formed by the chloride, bromide, and iodide radicals, Cl', Br', and I', are called *halogen salts*. The fluorides are often classed with these salts, and the cyanides show certain resemblances to them. There are a few complex radicals formed by the halogens and cyanogen, *e.g.*, PtCl₆'', chloroplatinate, Fe(CN)₆'', ferricyanide, Fe(CN)₆'', ferrocyanide, SiF₆'', fluosilicate, etc. The salts which these radicals form may be regarded as double salts which are not readily decomposed by water, as has already been stated in regard to ferrocyanides and ferricyanides,* *e.g.*,



It is to be noticed, however, that oxygen salts and sulphur salts may be formed by the combination of oxides and sulphides, *e.g.*,



so that there is a resemblance between these various kinds of salts. In fact, the analogy of K₂PtCl₆ and Na₂SiF₆ to K₂CO₃ and Na₂SiO₃, etc., is evident if two univalent chlorine

* See p. 82.

or fluorine atoms are regarded as playing the part of a bivalent oxygen atom.

The lithium, sodium, and potassium salts are often called *alkali-metal salts*. The ammonium salts show many resemblances to the latter and are often classed with them. Barium, calcium, magnesium, and strontium are referred to as *alkali-earth metals*. Aluminium is called an *earth metal*, while most of the other metals considered in this book are called *heavy metals*.

CHAPTER XXI.

CHEMICAL EQUATIONS.

IN order that the equation of a chemical reaction may be properly written, it is necessary to know what substances enter into the reaction and what are all its products.

In the equations given in this chapter, the following conventional signs will be used:

A line will be placed UNDER the formulas of solids and precipitates.

A line will be placed OVER the formulas of gases or vapors.

Formulas NOT marked as above will indicate that the substance is in solution.

For example, $\underline{\text{BaCO}_3} + \text{H}_2\text{SO}_4 = \underline{\text{BaSO}_4} + \text{H}_2\text{O} + \overline{\text{CO}_2}$ indicates that solid (precipitated) barium carbonate when acted upon by sulphuric acid in solution gives solid barium sulphate, water is formed, and carbon dioxide is evolved as a gas. The equation $\text{Ba}(\text{OH})_2 + \overline{\text{CO}_2} = \underline{\text{BaCO}_3} + \text{H}_2\text{O}$ indicates that carbon dioxide gas when passed into a solution of barium hydroxide gives a precipitate of barium carbonate, with the formation of water.

It must be distinctly understood that *chemical equations represent definite relative quantities of the substances reacting and formed.* For example, the equation $\overline{\text{NH}_3} + \overline{\text{HCl}} = \underline{\text{NH}_4\text{Cl}}$ does not merely show that ammonia and hydrogen chloride gases unite to form solid ammonium chloride, but it also shows that *one molecule* of NH_3 combines with *one mole-*

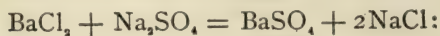
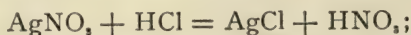
cule of HCl to form *exactly a molecule* of NH_4Cl , 17 parts by weight of ammonia and 36.5 parts of hydrochloric acid combining to form 53.5 parts of ammonium chloride.

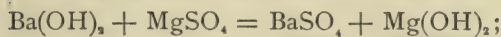
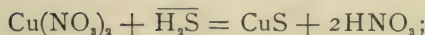
Since matter cannot be created or destroyed by chemical action, *the same number of atoms must occur upon both sides of an ordinary equation, i.e., one in which all the signs are plus.* If the foregoing rule is heeded, and if the substances reacting and formed are known, the writing of chemical equations is a very simple problem.

Equations involving Exchanges of Radicals.—The greater number of reactions that are made use of in qualitative analysis simply involve exchanges of radicals in solution. These exchanges depend upon ionization, and in writing reactions which are general with many salts, it is often convenient to make use of the symbols representing ions. Thus, $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$, shows that solutions of any silver salt and any chloride when mixed (in neutral or acid solution) give a precipitate of silver chloride; $\text{Ba}^{++} + \text{SO}_4^{--} = \text{BaSO}_4$ shows the precipitation of barium sulphate when solutions of barium salts and sulphates are mixed; $2\text{H}^+ + \text{CO}_3^{--} = \text{CO}_2 + \text{H}_2\text{O}$ shows that acids decompose carbonates with the evolution of carbon dioxide. (The last equation is not true for very weak acids, like hydrocyanic, HCN.) These simple equations, although very useful for generalizations, do not show all the products of a reaction. Hence, in special cases, it is usually preferable to make use of molecules in expressing reactions by means of equations, but the fact that the reactions depend upon ionization should not be lost sight of.

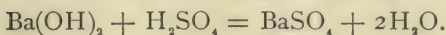
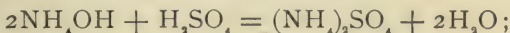
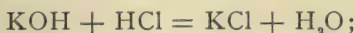
Some examples will now be given of equations which illustrate several kinds of reactions involving exchanges of radicals.

(a) Precipitates are formed:

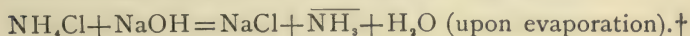
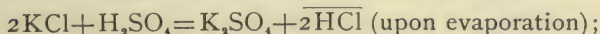
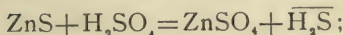
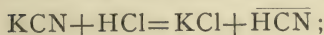
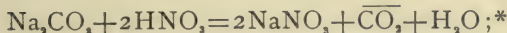




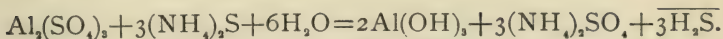
(b) Alkalies and acids neutralize each other, with or without the formation of precipitates:



(c) Gases are formed at once, or volatile products are formed upon evaporation. Neutralization also takes place:



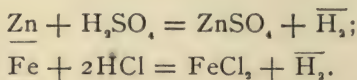
In some instances, it happens that one of the products that a change of radicals would produce cannot exist in the presence of water, and the result is therefore modified by the action of that liquid. Thus, aluminium sulphide cannot exist in the presence of water, even in an alkaline solution, so that the reaction of ammonium sulphide with an aluminium salt produces a precipitate of aluminium hydroxide (mixed with some basic salt):



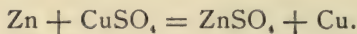
* H_2CO_3 is not stable, but decomposes into CO_2 and H_2O .

† NH_4OH decomposes into NH_3 and H_2O .

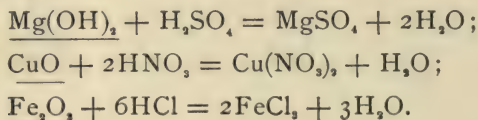
Equations involving the Replacement of Radicals.—Ions in a solution may be often replaced by other ions of the same sign, derived from a solid substance with which the solution is in contact. Thus, certain acids dissolve certain metals, metallic ions replacing those of hydrogen, which escape in the molecular condition:



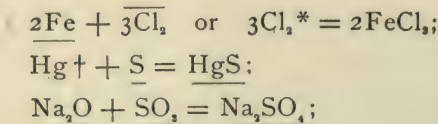
When solutions of salts of certain metals act upon certain other metals in the solid state (the latter being more strongly electropositive than the former), an exchange takes place, *e.g.*,



The ions of acids frequently act upon solid metallic oxides or hydroxides, dissolving them with the formation of a salt of the metal and water:

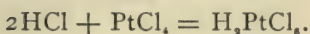
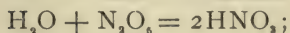
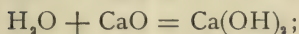
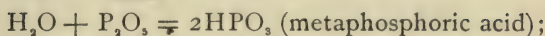
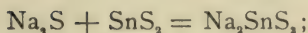


Equations involving Combinations.—Many elements, oxides, etc., combine with one another to form salts, acids, hydroxides, etc.:



* The chlorine may act in solution in water or in the gaseous state at an elevated temperature.

† Liquid.



Equations of Reactions involving Changes in the Radicals.

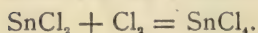
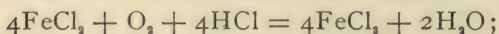
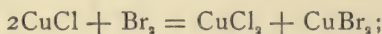
—The reactions now to be considered, which produce changes in the radicals themselves, are, in some instances, more complicated than those which involve only exchanges and replacements of radicals.

It is to be noticed that certain atoms occur in several radicals, either with the valence of the atom apparently unchanged or entirely different. Thus, the copper atom gives two radicals Cu^\cdot and $\text{Cu}^{\cdot\cdot}$; the mercury atom gives Hg^\cdot and $\text{Hg}^{\cdot\cdot}$; the iron atom occurs as $\text{Fe}^{\cdot\cdot}$ and $\text{Fe}^{\cdot\cdot\cdot}$, and exists apparently with the same valences in the negative groups $\text{Fe(CN)}_6'''$ and $\text{Fe(CN)}_6''''$; manganese gives the positive radical $\text{Mn}^{\cdot\cdot}$ and the negative radicals MnO_4'' and MnO_4' ; tin occurs in the positive radicals $\text{Sn}^{\cdot\cdot}$ and $\text{Sn}^{\cdot\cdot\cdot\cdot}$, and the negative radicals SnO_3'' , and SnS_3'' ; the chromium atom exists in $\text{Cr}^{\cdot\cdot\cdot}$, CrO_4'' and $\text{Cr}_2\text{O}_7''$; sulphur forms the negative radicals S'' , SO_3'' , and SO_4'' ; and nitrogen is present in NH_4' , NO_2' , and NO_3' .

In many cases, the changes that take place in converting one radical into another are most readily understood by considering what is called the "*state of oxidation*" of the atoms; that is, comparing the oxides which the positive radicals would form according to their valence, and determining from what oxides (or sulphides) the salts of the negative radicals may be formed. For example, ferrous and ferric oxides are FeO and Fe_2O_3 , and their salts correspond to these states of oxidation. Ferrous oxide may be changed to ferric by heating in contact with air; thus, $2\underline{\text{FeO}} + \bar{\text{O}} = \underline{\text{Fe}_2\text{O}_3}$.

The same amount of oxygen will also change a ferrous salt to a ferric; thus, $2\text{FeCl}_2 + \text{O} + 2\text{HCl} = 2\text{FeCl}_3 + \text{H}_2\text{O}$. The oxides corresponding to MnO_4'' and MnO_4' are determined by taking the formula of their acids, H_2MnO_4 and HMnO_4 (or any of their salts), and deducting the formula of water, H_2O (or the oxide of the metal forming the salt). This gives MnO_2 and Mn_2O_3 .

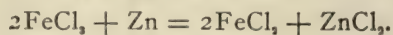
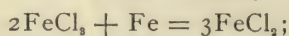
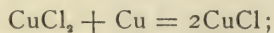
Cuprous, mercurous, ferrous, and stannous salts are changed to cupric, mercuric, ferric, and stannic salts, respectively, by so-called "oxidizing agents." These are able to form or give up negative ions. Thus, chlorine, bromine, oxygen, etc., in the molecular condition may produce these changes:



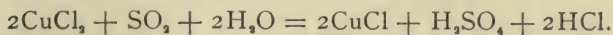
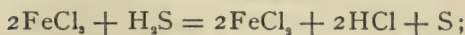
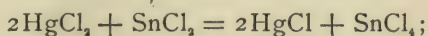
Substances which readily give up negative ions or oxygen may produce similar changes, *e.g.*,



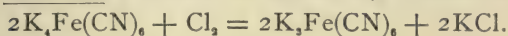
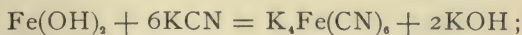
in which stannous chloride is changed to stannic chloride by the fact that mercuric chloride gives up one half of its chlorine. The mercuric chloride, of course, undergoes a change in the opposite direction at the same time, forming mercurous chloride. A change of the latter kind is called a reducing action, the reducing agent being one which removes negative ions, thus diminishing the valence of a positive atom. Metals in the solid state frequently act as reducing agents upon salts in solution:



Other readily oxidized substances may also act as reducing agents:

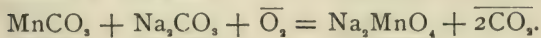
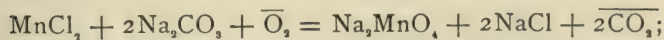


The formation of the ferrocyanogen radical may take place by ionic interchange, accompanied by the addition of a cyanide, while a ferricyanide may be produced by the action of an oxidizing agent on a ferrocyanide:

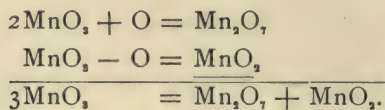


There are no simple reactions in solution which will produce the opposite changes and give ordinary ferrous and ferric salts from ferro- and ferricyanides, because the iron atoms are not ionized in a separate condition in the latter compounds.

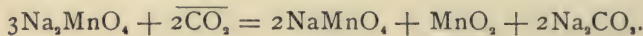
The change of a manganese salt to a manganate or permanganate requires oxidation, and in order to decide what amount of oxygen is necessary to effect the change, it is most convenient to compare the "state of oxidation" of the atom under the different conditions. The oxide of Mn^{++} is, of course, MnO ; the oxide of H_2MnO_4 is MnO_3 . It is therefore evident that two atoms of oxygen are necessary in changing a manganous salt to a manganate, and since a manganate may be made by igniting a manganese salt with an alkaline carbonate in presence of air, the following equations show the formation of sodium manganate from manganese chloride and from manganese carbonate:



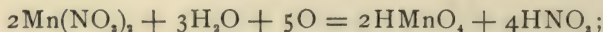
The oxides of a permanganate, *e.g.*, 2KMnO_4 , are K_2O and Mn_2O_7 . The solution of a manganate readily decomposes into a permanganate, with the precipitation of manganese dioxide, MnO_2 , especially under the influence of carbon dioxide, CO_2 . In order to write the equation of the latter reaction, it is convenient to find the amount of oxygen gained and lost by MnO_3 in forming Mn_2O_7 and MnO_2 ; thus, $2\text{MnO}_3 + \text{O} = \text{Mn}_2\text{O}_7$, and $\text{MnO}_3 - \text{O} = \text{MnO}_2$. The gain and loss of oxygen may be eliminated by addition; thus,



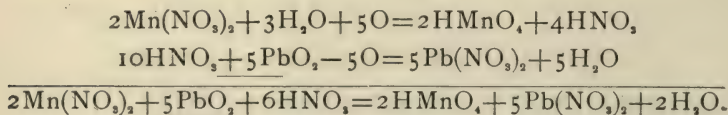
The result then shows the proportions in which the substances must react, and the complete equation is readily written, as follows:



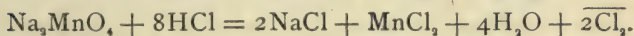
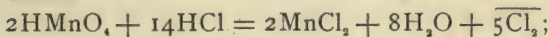
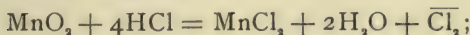
Permanganic acid may be produced by boiling a dilute solution of a manganese salt in nitric acid with lead dioxide, PbO_2 . The lead dioxide gives up one half of its oxygen, and forms lead nitrate: $\text{PbO}_2 - \text{O} + 2\text{HNO}_3 = \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$. To change 2MnO to Mn_2O_7 requires 5 atoms of oxygen. This leads to the equation



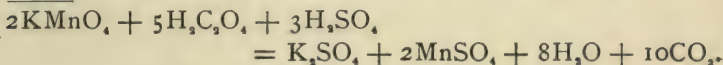
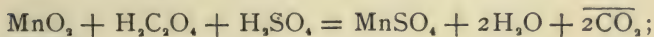
or, if the lead dioxide is to be included, the previous equation may be multiplied by 5 and added to the last, as follows:



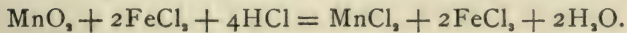
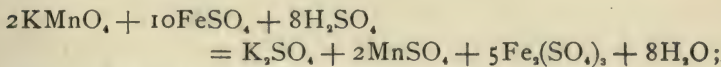
The manganese of manganates and permanganates, as well as that of other higher oxides, may be converted into manganese salts in various ways, in all of which oxygen is removed. Hydrochloric acid, especially when strong and warm, produces this result. The amount of hydrochloric acid required in such an equation is readily determined if it is considered that each atom of available oxygen (*i.e.*, the oxygen in excess of MnO) with 2 molecules of hydrochloric acid yields 1 molecule of water and 2 atoms of chlorine ($\text{O} + 2\text{HCl} = \text{H}_2\text{O} + \overline{\text{Cl}_2}$), and that the MnO and other oxides present (excepting water) are converted into chlorides ($\text{MnO} + 2\text{HCl} = \text{MnCl}_2 + \text{H}_2\text{O}$). The following equations furnish examples of this action:



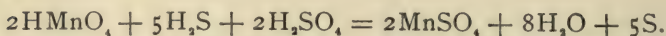
Oxalic acid, in warm solutions, in the presence of sulphuric acid reduces the higher oxides of manganese, 1 atom of the available oxygen oxidizing a molecule of oxalic acid ($\text{O} + \text{H}_2\text{C}_2\text{O}_4 = \text{H}_2\text{O} + \overline{2\text{CO}_2}$):



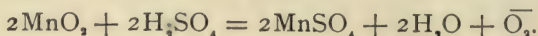
Ferrous salts in acid solutions, even when cold, also reduce the higher oxides of manganese, 2 atoms of ferrous iron taking up 1 atom of available oxygen ($2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$):



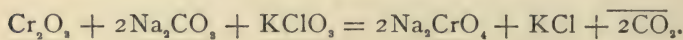
Hydrogen sulphide also reduces the higher oxides of manganese in acid solutions, *e.g.*,



Hot, concentrated sulphuric acid decomposes the higher oxides of manganese, with the evolution of oxygen, *e.g.*,



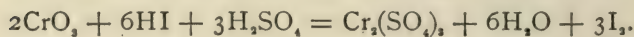
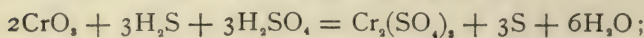
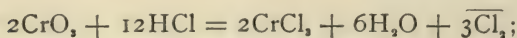
The chromium of a chromium salt is converted into the chromate radical by oxidation. The two oxides are Cr_2O_3 and CrO_3 , so that 3 atoms of oxygen are required to effect the change of 2 chromium atoms. This is accomplished in the dry way by fusion with an alkaline hydroxide or carbonate and an oxidizing agent such as a chlorate or nitrate:



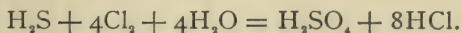
In the wet way, the same change is effected by the action of alkaline solutions of hypochlorites upon the precipitated hydroxide, *e.g.*,



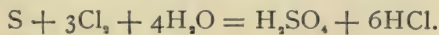
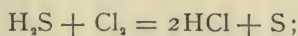
The opposite change, from chromates to chromium salts, is effected by reducing agents, such as hot hydrochloric acid, cold hydrogen sulphide water, or cold hydriodic acid (potassium iodide and sulphuric acid). The proportions required for the equations are evident when the amount of available oxygen is considered:



Sulphides are changed to sulphates by the action of oxidizing agents, for instance by chlorine in the presence of water:

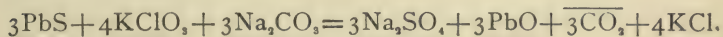


The reaction indicated by this equation, however, takes place in two steps, the hydrogen being attacked first and the sulphur afterwards:



If the last two equations are added, the preceding equation will be obtained. It is evident that the amount of chlorine necessary for the complete oxidation of hydrogen sulphide must be equivalent to the 4 atoms of oxygen in sulphuric acid, or, in other words, to the oxygen of the oxides H_2O and SO_2 , and 2 chlorines are equivalent to 1 oxygen.

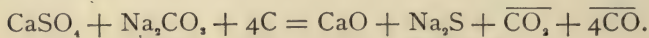
Sulphides are also converted into sulphates by fusion with oxidizing agents, usually in the presence of alkaline carbonates, *e.g.*,



In this equation, the oxides of lead and sulphur to be formed being PbO and SO_2 , the amount of oxygen required is evidently 4 atoms for each PbS ; and in order to obtain the proper amount of it from KClO_3 , which has 3 atoms of available oxygen, the proportions given in the equation must be taken. To write the equation properly, it must be known that lead sulphate is decomposed by fusing sodium carbonate, and that the resulting lead carbonate is decomposed by heat into lead oxide and carbon dioxide.

Sulphates are converted into sulphides by the action of powerful reducing agents. Fusion with an alkaline carbonate

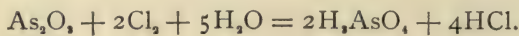
on charcoal is an example of an operation which produces this change:



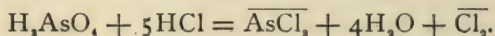
In order to write this equation properly, it is necessary to know that fusing sodium carbonate readily decomposes calcium sulphate by interchange of radicals, that calcium carbonate is decomposed at a high temperature into the oxides CaO and CO_2 , and that reductions at high temperatures in the presence of an excess of carbon cause the formation of CO rather than CO_2 .

Arsenious compounds are converted into compounds of higher valence by oxidizing agents, and the opposite change is readily brought about by reducing agents.

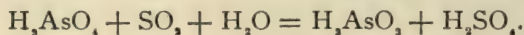
The arsenic atom has little tendency to act as a positive radical, especially in its higher valence (5), hence it usually forms the arsenate radical. For example, chlorine-water acts upon arsenious oxide, as follows:



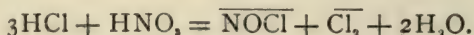
With concentrated, hot hydrochloric acid, a reaction in the opposite direction takes place to some extent:



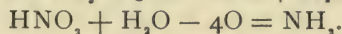
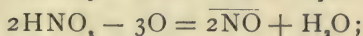
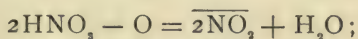
The reduction is readily effected by means of sulphur dioxide:



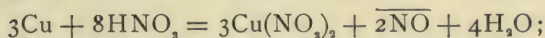
Among the commonly used oxidizing agents are *aqua regia* and *nitric acid*. The former is a mixture of hydrochloric and nitric acids which liberates chlorine according to the equation



Nitric acid readily gives up oxygen to substances, being itself reduced, according to its concentration, the temperature, and the energy of the action of the reducing agent employed, to NO_2 , N_2O_3 , NO , N_2O , or even to N_2 or NH_3 . It often happens that several of these reduction products of nitric acid are produced at the same time. The following equations show the amount of available oxygen furnished in producing several of the compounds mentioned:



Oxidation reactions in which nitric acid furnishes the oxygen may be readily written if the production of a certain compound of nitrogen is assumed. Thus, when metallic copper is dissolved in nitric acid, it is known that each atom of copper requires an atom of oxygen for oxidation, because its oxide is CuO . Moreover, each atom of copper requires 2 molecules of nitric acid to form copper nitrate ($\text{CuO} + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O}$). Hence the following equations may be constructed upon the suppositions that NO_2 , NO , and NH_3 are the products of reduction:



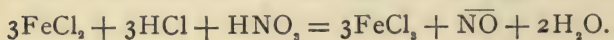
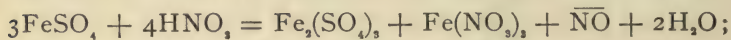
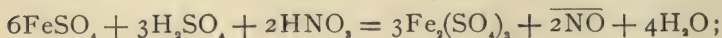
Other examples of the action of nitric acid are the solution (or oxidation) of sulphides, the change of ferrous to ferric salts, etc. For instance, concentrated hot nitric acid converts compact lead sulphide (pulverized galena) chiefly to lead sulphate:



On the other hand, hot dilute nitric acid with lead sulphide gives principally lead nitrate and separated sulphur:



The following equations show the conversion of ferrous to ferric salts:



PART III.

DESCRIPTIVE PART.

A BRIEF ACCOUNT OF THE PROPERTIES OF THE INORGANIC
RADICALS.*

CHAPTER XXII.

ALUMINIUM, Al^{\dots} . (FRESENIUS, p. 165.)

ALUMINIUM CHLORIDE is soluble in dilute hydrochloric acid solutions.

Hydrogen sulphide produces no precipitate in acid solutions. The sulphide is not formed in the wet way, even in alkaline solutions, so that *ammonium sulphide*, when added to solutions of soluble aluminium salts, produces precipitates of aluminium hydroxide, $\text{Al}(\text{OH})_3$, with the evolution of hydrogen sulphide.

Ammonium hydroxide produces precipitates of the hydroxide, $\text{Al}(\text{OH})_3$, which dissolves to a slight extent in a large excess of ammonium hydroxide, and dissolves readily in sodium (or potassium) hydroxide solution, especially when hot, forming sodium (or potassium) aluminate, $\text{Al}(\text{ONa})_3$. When the latter solution is acidified with hydrochloric acid, aluminium chloride and sodium chloride are formed, and, the

* The arrangement is alphabetical, according to the names of the radicals.

sodium hydroxide having been removed, ammonium hydroxide will now produce a precipitate of aluminium hydroxide.

If *sodium acetate*, $\text{NaC}_2\text{H}_3\text{O}_2$, is added in excess to a nearly neutral solution of an aluminium salt, and the latter is largely diluted with water, and boiled, a precipitate of basic aluminium acetate (the hydroxide combined with the acetate) is produced. Like the hydroxide, the basic aluminium acetate dissolves in boiling sodium hydroxide solution, and the resulting solution behaves in the same manner as that obtained from the hydroxide when it is acidified with hydrochloric acid and treated with ammonium hydroxide.

CHAPTER XXIII.

AMMONIUM, NH_4^+ . (FRESENIUS, p. 137.)

WHEN *calcium hydroxide*, $\text{Ca}(\text{OH})_2$, in the form of powder, is moistened with the solution of an ammonium salt, and the mixture is triturated, ammonia, NH_3 , is evolved. The ammonia may be recognized by its odor, or, if small in quantity, by allowing it to come in contact with the vapor of hydrochloric or acetic acid, or by detecting its action upon moistened test-papers, exposed upon the under side of a watch-glass covering the vessel in which the trituration has been made.

Sodium or potassium hydroxide solution also liberates ammonia from solutions of ammonium salts. If the solutions are dilute, it may be necessary to heat them to boiling before the ammonia can be detected.

All ammonium salts are *volatile*, or are decomposed with the loss of ammonium, when heated below redness.

Hydrochloroplatinic acid, H_2PtCl_6 , added to concentrated solutions of ammonium salts produces a yellow precipitate of ammonium chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$. Ammonium salts, therefore, must be *completely removed* before testing for potassium by means of this reagent.

CHAPTER XXIV.

ANTIMONY, $\text{Sb}^{\cdot\cdot\cdot}$, $\text{Sb}^{\cdot\cdot\cdot\cdot}$, etc.* (FRESENIUS, p. 271.)

ANTIMONIOUS and antimonious chlorides, SbCl_3 and SbCl_5 , are soluble in moderately dilute hydrochloric acid. When these solutions are diluted with water, or when hydrochloric acid is added to solutions of other antimony compounds, antimony oxychlorides, SbOCl , SbO_2Cl , etc., are frequently precipitated when the amount of acid present is not very large. These precipitates are dissolved by the further addition of hydrochloric acid.

From dilute acid solutions of antimonious salts or antimonites, *hydrogen sulphide* precipitates orange-colored antimonious sulphide, Sb_2S_3 ; while from acid solutions of antimonious salts and of antimonates, it produces a similar precipitate of antimonious sulphide, Sb_2S_3 .

The sulphides Sb_2S_3 and Sb_2S_5 dissolve in *yellow ammonium sulphide* solution, the former taking up two atoms of sulphur, and both forming ammonium thio-antimonate, $(\text{NH}_4)_2\text{SbS}_4$. Upon acidifying the solution of the latter com-

* The oxide Sb_2O_3 has weak acid properties, and several antimonites are known, for instance, $\text{NaSbO}_3 \cdot 3\text{H}_2\text{O}$. When dissolved in strong acids however, the antimonites give solutions of antimonious salts, such as SbCl_3 and $\text{Sb}_2(\text{SO}_4)_3$. The oxide Sb_2O_5 has somewhat stronger acid properties than the lower oxide, and forms various kinds of antimonates, corresponding to HSbO_3 , H_3SbO_4 , $\text{H}_4\text{Sb}_2\text{O}_7$, etc. (and analogous thio-salts exist). When these acids or their salts are dissolved in hydrochloric acid, the solutions apparently contain antimonious chloride, SbCl_3 , but oxygen salts of the radical $\text{Sb}^{\cdot\cdot\cdot\cdot}$, such as antimonious sulphate, etc., probably do not exist.

pound with hydrochloric acid, antimonious sulphide, Sb_2S_3 , is precipitated, with the evolution of hydrogen sulphide.

Antimonious and antimonious sulphides dissolve readily in *boiling hydrochloric acid* (the concentrated acid diluted with an equal volume of water), both yielding antimonious chloride, SbCl_3 , sulphur being separated in the case of antimonious sulphide.

When *metallic zinc* in contact with platinum foil is placed in a solution of antimonious chloride containing hydrochloric acid, metallic antimony is deposited as a black coating upon the platinum foil, while a part of the metal may form a precipitate which is suspended in the liquid or attached to the zinc. At the same time, a portion of the antimony escapes with the hydrogen in the form of hydrogen antimonide, SbH_3 . The metallic antimony precipitated by zinc does not dissolve in hydrochloric acid, except to a slight extent, which is due to the presence of atmospheric oxygen. It dissolves, however, in warm, dilute nitric acid, especially in the presence of tartaric acid.

CHAPTER XXV.

ARSENIC, As^{III} , $\text{AsO}_4^{\text{III}}$, etc.* (FRESENIUS, pp. 278 and 291.)

IN acid solutions of arsenious salts or arsenites, *hydrogen sulphide* produces a yellow precipitate of arsenious sulphide, As_2S_3 . Upon dilute acid solutions of arsenates, it acts very slowly when cold, more rapidly when heated to about 70°C ., but immediately upon cold solutions containing a very large amount of hydrochloric acid (about two volumes of the concentrated acid to one volume of the liquid), producing arsenic sulphide, As_2S_5 , or sometimes a mixture of As_2S_3 and S_8 .

The sulphides As_2S_3 and As_2S_5 dissolve very readily in *yellow ammonium sulphide*, the former taking up two atoms of sulphur, and both forming ammonium thio-arsenate, $(\text{NH}_4)_2\text{AsS}_4$. When the solution of the latter salt is acidified with hydrochloric acid, arsenic sulphide, As_2S_5 , is precipitated and hydrogen sulphide is evolved.

The sulphides of arsenic are practically insoluble in boiling hydrochloric acid.

The sulphides of arsenic are decomposed, with the separation of sulphur and the formation of soluble arsenic acid, when treated with *boiling nitric acid* (equal volumes of the concentrated acid and water or stronger).

* The positive radical As^{III} is known in combination with but few negative radicals, such as oxygen, sulphur, and the halogens. The oxide As_2O_3 is a rather strong acid anhydride, forming various types of salts which correspond to the acids H_3AsO_3 , $\text{H}_4\text{As}_2\text{O}_5$, HAsO_2 , etc. The oxide As_2O_5 has strong acid properties, forming orthoarsenates, pyroarsenates, and metarsenates, corresponding to the acids H_3AsO_4 , $\text{H}_4\text{As}_2\text{O}_7$, and HAsO_3 .

If a liberal amount of *silver nitrate* solution (an excess of this reagent increases the delicacy of the reaction) is added to a solution of arsenic acid in nitric acid, any silver chloride accidentally produced is filtered off, the solution is almost neutralized in a test-tube with ammonium hydroxide, and finally the upper part of the liquid is made slightly alkaline with this reagent, while the lower part remains slightly acid, a precipitate of silver arsenate, Ag_3AsO_4 , will be formed in the neutral zone between the two liquids.

CHAPTER XXVI.

BARIUM, Ba⁺⁺. (FRESENIUS, p. 147.)

BARIUM CHLORIDE,* sulphide, and hydroxide are soluble in water, hence they do not form precipitates.

Barium phosphate, oxalate, borate, and silicate are soluble in hydrochloric or nitric acid, but they are insoluble, or, in some cases, nearly insoluble in water in the presence of neutral or alkaline compounds. Upon neutralizing an acid solution, ammonium hydroxide may therefore precipitate these barium salts, if the radicals which form them are present. When barium phosphate, oxalate, borate, or silicate is dissolved in hydrochloric acid, an excess of ferric chloride added, the solution neutralized as far as possible with sodium carbonate without producing a permanent precipitate, an excess of sodium acetate added, and the liquid largely diluted and then boiled, ferric phosphate, oxalate, borate, or silicate is precipitated together with basic ferric acetate, and the barium remains in solution as barium chloride or acetate. Upon removing the precipitate by filtration and making the filtrate alkaline with ammonium hydroxide, the barium will remain in solution if the previous operations have been properly conducted.

Ammonium carbonate (and other soluble carbonates) added to solutions of barium salts gives a precipitate of barium carbonate, BaCO₃. The presence of ammonium hydroxide aids

* Barium chloride is sparingly soluble in strong solutions of hydrochloric acid. Hence it may be partially precipitated by the addition of a large quantity of that acid when comparatively little water is present.

this precipitation by its tendency to prevent the formation of acid barium carbonate, $\text{Ba}(\text{HCO}_3)_2$. Ammonium chloride (or other ammonium salts) tends to make the precipitation of barium carbonate incomplete, but it is necessary to have this salt present in separating barium from magnesium.

Barium carbonate dissolves readily in hydrochloric acid mixed with water, with the formation of barium chloride, BaCl_2 , and the evolution of carbon dioxide, CO_2 . Upon evaporating the resulting solution to complete dryness, the excess of hydrochloric acid used is removed, and by treating the residue with water, a neutral solution of barium chloride may be obtained.

When *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, in excess, and a liberal amount of *sodium acetate*, $\text{NaC}_2\text{H}_3\text{O}_2$, are added to a neutral solution of barium chloride, the barium is completely precipitated as barium chromate, BaCrO_4 . It is best to make this precipitation in a boiling solution, because the precipitate filters better when so treated. The presence of acids is to be avoided, except in very minute quantities. Acetic acid in very small amount has no injurious influence, and this acid is liberated when the sodium acetate is added to a solution that contains traces of a stronger acid. The chromic acid, H_2CrO_4 , liberated by the reaction has no solvent action upon the precipitate.

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, added to solutions containing even very minute quantities of barium salts, produces precipitates of barium sulphate, BaSO_4 . The precipitate is also produced by other soluble sulphates, in neutral, acid, or alkaline solutions. Barium sulphate is decomposed by fusion with sodium carbonate, and upon treating the mass with water and filtering, barium carbonate remains as a residue, while sodium sulphate is found in the filtrate. The same result is finally obtained by repeatedly boiling barium sulphate with fresh portions of strong sodium carbonate solution.

CHAPTER XXVII.

BISMUTH, Bi⁺⁺⁺. (FRESENIUS, p. 244.)

BISMUTH CHLORIDE, BiCl₃, is soluble in dilute hydrochloric acid. The addition of water to this solution usually produces a precipitate of basic bismuth chloride, BiOCl, which dissolves upon the addition of a sufficient quantity of hydrochloric acid.

Hydrogen sulphide, H₂S, added to moderately acid solutions of bismuth salts, produces a black precipitate of bismuth sulphide, Bi₂S₃. This is insoluble in yellow ammonium sulphide. It dissolves in boiling dilute nitric acid, with the formation of bismuth nitrate, Bi(NO₃)₃, and the separation of sulphur.

By evaporation with an excess of sulphuric acid, bismuth nitrate (like all other nitrates) is converted into sulphate. The sulphate thus obtained, Bi₂(SO₄)₃, dissolves in water containing a considerable amount of sulphuric acid, but if too little of the acid is present, the basic salt Bi₂O₃.SO₃ is precipitated, while, upon standing, the more acid solution often deposits the basic salt Bi₂O₃(SO₄)₂.3H₂O.

Ammonium hydroxide added in excess to the solution of a bismuth salt produces a white precipitate of bismuth hydroxide, BiOOH.

When bismuth hydroxide is treated upon the filter with a solution of *sodium stannite*, Na₂SnO₃, black bismuthous oxide, BiO, is formed. (The sodium stannite is prepared by adding an excess of sodium hydroxide to a little stannous chloride, SnCl₂, solution.)

CHAPTER XXVIII.

BORATES, BO_3''' , BO_3' , $\text{B}_4\text{O}_7''$, etc.* (FRESENIUS, p. 334.)

THE various borates dissolve in acids, and, upon evaporating the acid solutions, orthoboric acid gradually escapes with the water-vapor. If a solution contains an excess of sodium or potassium hydroxide or carbonate, it may be evaporated and the residue ignited without loss of boric acid.

When *turmeric-paper* is moistened with a not too dilute solution of a borate in dilute hydrochloric acid, and dried at 100° , it assumes a peculiar red color. The presence of free sulphuric acid interferes with this test, because this acid chars the paper under the conditions of the experiment. If sulphuric acid is present, therefore, it must be neutralized with sodium or potassium carbonate or hydroxide, and then, after acidifying the solution with hydrochloric acid, the test may be applied. Chloric acid interferes with the test, because it bleaches the test-paper; hence chlorates, if present, should be previously destroyed by igniting the salts, after adding sodium carbonate, if necessary, to prevent the loss of boric acid. Ferric salts, and some other compounds, may change the color of turmeric-paper. When such salts are present, it is best to fuse the substance with sodium carbonate, treat with water, filter, and apply the test to the acidified filtrate.

* All the various borates are derived from the oxide B_2O_3 , and the acids corresponding to the radicals given here may be supposed to be formed by the union of this oxide with water, as follows: Orthoboric acid, $\text{B}_2\text{O}_3 + 3\text{H}_2\text{O} = 2\text{H}_3\text{BO}_3$; metaboric acid, $\text{B}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HBO}_2$; tetraboric or pyroboric acid, $2\text{B}_2\text{O}_3 + \text{H}_2\text{O} = \text{H}_2\text{B}_4\text{O}_7$.

CHAPTER XXIX.

BROMIDES, Br'. (FRESENIUS, p. 357.)

BARIUM BROMIDE and cadmium bromide are soluble in water, hence they do not form precipitates.

Neither hydrobromic acid nor bromine is given off upon boiling the solution of a bromide with acetic acid (stronger acids being absent), even in the presence of nitrates and chlorates.

In neutral and acid solutions of bromides, *silver nitrate* produces a pale yellow precipitate of silver bromide, AgBr. When washed free from silver nitrate, the precipitate dissolves somewhat sparingly in a mixture of 3 volumes of strong ammonium nitrate solution and 1 volume of ammonium hydroxide of .94 sp. gr. The addition of an equal volume of 5 per cent *silver nitrate* solution reprecipitates all the silver bromide from this solution, unless much silver chloride is also present. The addition of *nitric acid* to acid reaction also precipitates the silver bromide from this ammoniacal solution.

When silver bromide is suspended in a little water, and *metallic zinc* and a little dilute *sulphuric acid* are added, the compound is decomposed upon agitation, with the formation of black metallic silver and soluble hydrobromic acid or zinc bromide.

When *chlorine-water* is added to the acid solution of a bromide (containing sulphuric acid), bromine is set free. If a little *carbon disulphide* is added at the same time, this sol-

vent assumes a reddish-yellow color, on account of bromine dissolving in it. The chlorine-water should be added gradually, with agitation of the liquids, until it is certain that an excess is present. A very large excess of chlorine-water causes the formation of chlorides of bromine and weakens the color.

CHAPTER XXX.

CADMIUM, Cd^{++} . (FRESENIUS, p. 247.)

CADMIUM CHLORIDE is very soluble in water, and hence it cannot form a precipitate upon the addition of hydrochloric acid to solutions of cadmium salts.

In acid solutions of cadmium salts, provided *not too much* free acid is present, *hydrogen sulphide* produces a bright yellow precipitate of cadmium sulphide, CdS . The precipitate is insoluble in yellow ammonium sulphide. It dissolves in boiling dilute nitric acid, with the formation of cadmium nitrate, $\text{Cd}(\text{NO}_3)_2$, and the separation of sulphur. It also dissolves in boiling dilute sulphuric acid, with the formation of cadmium sulphate and the evolution of hydrogen sulphide. Cadmium sulphide is insoluble in potassium cyanide solution.

Upon the evaporation of its solution with an excess of sulphuric acid, cadmium nitrate is converted into the sulphate. The latter is readily soluble in water.

When an excess of ammonium hydroxide is added to the solution of a cadmium salt, any precipitate which may be formed at the neutral point (cadmium hydroxide) is redissolved, and a colorless solution results, containing salts of the cadmium-ammonia bases, *e.g.*, $\text{Cd}(\text{NH}_3)_4\text{SO}_4$.

CHAPTER XXXI.

CALCIUM, Ca^{++} . (FRESENIUS, p. 153.)

CALCIUM salts give no precipitates with hydrochloric acid or hydrogen sulphide. Those calcium salts which are soluble in water give solutions in which neither ammonium hydroxide nor ammonium sulphide produces precipitates; but solutions of calcium phosphate, oxalate, borate, fluoride, or silicate in hydrochloric or nitric acid give precipitates of these compounds when the acid is neutralized with ammonium hydroxide or sulphide. Calcium may be separated from the phosphate, oxalate, borate, and silicate radicals in the same manner as barium (see p. 108).

Ammonium carbonate added to solutions of calcium salts gives a precipitate of calcium carbonate, CaCO_3 . The presence of ammonium hydroxide aids this precipitation by its tendency to prevent the formation of acid calcium carbonate, $\text{Ca}(\text{HCO}_3)_2$. Ammonium chloride tends to make the precipitation of calcium carbonate incomplete, but it is necessary to have an ammonium salt present in separating calcium from magnesium.

Calcium carbonate dissolves readily, both in hydrochloric and in nitric acid. Upon evaporating the resulting solutions to dryness, the solid salts may be obtained.

Potassium dichromate produces no precipitate when added with sodium acetate to the neutral solution of a calcium salt. From such a solution made alkaline with ammonium hydroxide, and containing a calcium salt and also chromates, ammonium carbonate precipitates calcium carbonate.

When a very concentrated solution of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is boiled with an excess of *amyl alcohol* until the water has disappeared, and further until the amyl alcohol has become anhydrous, the calcium nitrate dissolves in the amyl alcohol. Upon evaporating off the amyl alcohol, solid calcium nitrate is left as a residue.

When *ammonium oxalate* solution is added, even to a very dilute, neutral or alkaline solution of a calcium salt, a finely pulverulent, white precipitate of calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ or $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, is produced. This precipitate is also formed in solutions acidified with acetic acid, but in this case the reaction is less delicate, especially if the amount of acetic acid present is considerable.

CHAPTER XXXII.

CARBONATES, CO_2 ". (FRESENIUS, p. 347.)

SOLID carbonates dissolve in *acids*, with effervescence of carbon dioxide, CO_2 , a colorless and practically odorless gas. Almost any acid will answer the purpose in most cases, but certain carbonates, like magnesite and dolomite, require the use of the more powerful acids with the aid of heat. An acid should be used which does not form an insoluble salt with the metallic radical of the carbonate, and dilute acids rather than concentrated ones should usually be employed, because many salts are difficultly soluble in the strong acids to which they correspond, so that the action of the latter upon a carbonate may be very slight, or even imperceptible.

The solutions of the carbonates which are soluble in water (*i.e.*, ammonium, lithium, sodium, and potassium carbonates) give off carbon dioxide when acids are added to them, provided that they are not so dilute that all the gas produced remains dissolved in the water present. The solubility of the gas decreases rapidly as the temperature rises, so that the test is more delicate in hot solutions than in cold ones.

When carbon dioxide or air containing that gas is passed into a solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$, a precipitate of calcium carbonate, CaCO_3 , is formed. This test furnishes a means for detecting carbon dioxide in the presence of other effervescing gases, such as hydrogen cyanide and sulphide, and also for detecting small quantities of the gas under consideration. It is usually convenient to place the substance or the solution in a distilling-bulb, to connect the tube of the

latter with a delivery-tube passing into a test-tube containing the calcium hydroxide solution, then, after adding an acid to the contents of the distilling-bulb, to cork the neck of the latter, and apply heat until the liquid boils, if necessary. It should be noticed that an excess of carbon dioxide will redissolve the precipitate of calcium carbonate, forming the acid carbonate, $\text{Ca}(\text{HCO}_3)_2$.

CHAPTER XXXIII.

CHLORATES, ClO_3' . (FRESENIUS, p. 390.)

ALL the chlorates are soluble in water, hence none of them forms a precipitate in moderately dilute solutions.

If a small quantity of a dry chlorate is treated with a few drops of *concentrated sulphuric acid*, the chloric acid, HClO_3 , set free, at once decomposes* into perchloric acid, HClO_4 , and chlorine peroxide, ClO_2 , the latter imparting to the sulphuric acid an intense yellow color, and also betraying its presence by a powerful and disagreeable odor. Chlorine peroxide is exceedingly explosive, and should be produced only in very small quantities.

Chlorates are decomposed by *ignition*, forming chlorides and evolving oxygen. If a substance contains no chlorides or other acid radicals of the same group, or if such acid radicals have been removed by the addition of an excess of silver nitrate to the solution, the chlorate may be converted into chloride by ignition, and the detection of the latter will show the previous presence of a chlorate. Where a solution is to be evaporated in order that the residue may be ignited, it must be made alkaline with sodium carbonate or some other alkaline substance in order that the chloric acid may not be lost by volatilization.



CHAPTER XXXIV.

CHLORIDES, Cl'. (FRESENIUS, p. 355.)

BARIUM CHLORIDE and cadmium chloride are soluble in water, hence precipitates are not produced by adding a barium salt or a cadmium salt to the dilute solution of a chloride.

Neither hydrochloric acid nor chlorine is lost upon boiling the solution of a chloride with an excess of acetic acid, provided that no stronger acid is present in the free state, even in the presence of nitrates and chlorates.

In neutral and acid solutions of chlorides, *silver nitrate* produces a white, curdy precipitate of silver chloride, AgCl , which darkens upon exposure to daylight. The precipitate dissolves readily in a mixture of 3 volumes of strong ammonium nitrate solution and 1 volume of *ammonium hydroxide* of .94 sp. gr. Upon adding an *exactly* equal volume of 5 per cent *silver nitrate* solution to this ammoniacal solution of silver chloride, a *part* of the silver chloride may be precipitated if much is present, but a part will remain in solution. Acidifying the ammoniacal solution with *nitric acid*, either after the addition of silver nitrate or without this addition, will reprecipitate all the silver chloride.

When silver chloride is suspended in a little water, and *metallic zinc* and a small quantity of dilute *sulphuric acid* are added, the compound is decomposed, upon thorough agitation, with the formation of black metallic silver and soluble chlorides.

CHAPTER XXXV.

CHROMATES, $\text{CrO}_4^{''}$. (FRESENIUS, p. 317.)

CHROMIUM, Cr^{+++} . (FRESENIUS, p. 168.)

MOST of the chromates dissolve either in water or in acids. Their neutral or alkaline solutions (normal chromates) have a yellow color, while acid solutions (dichromates or chromic acid) have an orange tint. These colors are so powerful that, in absence of other colored bodies, they furnish a delicate means of detecting the compounds. In acid solutions of chromates, hydrogen sulphide produces chromium salts, with the separation of sulphur, a characteristic change of color from orange to green taking place. For example, in the presence of hydrochloric acid, chromic chloride, CrCl_3 , is produced.

Solutions of chromium salts do not give precipitates with hydrochloric acid or with hydrogen sulphide in acid solutions.

Ammonium hydroxide added to solutions of chromium salts gives a grayish-green or sometimes a grayish-blue precipitate of chromic hydroxide, $\text{Cr}(\text{OH})_3$. The liquid should be boiled, in order to make the precipitation complete. The precipitate is insoluble in boiling sodium or potassium hydroxide solution, but it may dissolve in the cold solution. It dissolves in the stronger acids. It dissolves also in boiling sodium hypochlorite solution in the presence of sodium hydroxide, with the formation of a yellow solution containing sodium chromate, Na_2CrO_4 . The addition of an acid to the latter solution deepens its color to orange.

If *sodium acetate* is added in excess to a nearly neutral solution of a chromium salt, and this is largely diluted with water and boiled, a precipitate of basic chromium acetate (the hydroxide combined with the acetate) is produced. With solutions of sodium hydroxide and sodium hypochlorite, this basic acetate behaves like the hydroxide.

CHAPTER XXXVI.

COBALT, Co⁺⁺. (FRESENIUS, p. 202.)

SOLUTIONS of cobalt salts do not give precipitates with hydrochloric acid, with hydrogen sulphide in acid solutions, nor with ammonium hydroxide in the presence of ammonium chloride.

With *ammonium sulphide*, a black precipitate of cobalt sulphide, CoS, is produced. The precipitate is practically insoluble in a cold mixture of 1 volume of pure dilute hydrochloric acid and 3 volumes of hydrogen sulphide water. It is best to wash the precipitate before treating it with this mixture, because in the presence of nitrates its solubility may be increased from the formation of aqua regia. Cobalt sulphide dissolves readily in warm aqua regia, with the formation of cobalt chloride, nitrate, or sulphate, and usually with the partial separation of the sulphur. When the aqua regia solution is evaporated to dryness, the residue, if not heated too strongly, dissolves in water, giving a solution containing but little free acid.

When a concentrated solution of a cobalt salt containing but little free acid is treated with a little *acetic acid*, and a large excess of solid *potassium nitrite* is dissolved in it, a yellow precipitate of potassium cobaltic nitrite, $K_2Co(NO_2)_6 \cdot 3H_2O$, is produced. If the mixture is allowed to stand for several hours in a warm place, the precipitation of cobalt is complete under the proper conditions.

The *borax bead* is colored intensely blue by cobalt compounds.

CHAPTER XXXVII.

CUPRIC SALTS, Cu^{++} . (FRESENIUS, p. 240.)

CUPRIC CHLORIDE is soluble in water, hence the addition of hydrochloric acid to solutions of cupric salts does not produce a precipitate.

In neutral or acid solutions of cupric salts, *hydrogen sulphide* produces a black precipitate of cupric sulphide, CuS , usually containing cuprous sulphide, Cu_2S , and sulphur. The precipitate is insoluble, except to a very slight degree, in yellow ammonium sulphide. It dissolves in boiling dilute nitric acid, with the formation of cupric nitrate and the separation of sulphur. It dissolves readily in potassium cyanide solution.

When a solution of cupric nitrate is evaporated with an excess of sulphuric acid, cupric sulphate, which is soluble in water, is produced.

When *ammonium hydroxide* is added in excess to the solution of a cupric salt, any precipitate (of hydroxide) that may be produced at the point of neutrality is redissolved, and an azure-blue solution is formed, containing one or more copper-ammonia salts, *e.g.*, $\text{Cu}(\text{NH}_3)_4\text{SO}_4$.

CHAPTER XXXVIII.

CYANIDES, CN'. (FRESENIUS, p. 364.)

SOLUBLE cyanides are decomposed by acids, even by *acetic acid*, with the evolution of hydrogen cyanide (Poison!).

In acid solutions of cyanides, *silver nitrate* produces a white precipitate of silver cyanide, AgCN.

If small quantities of a ferric and a ferrous salt are added to the solution of a cyanide, it is then made alkaline with sodium or potassium hydroxide, and finally acidified with hydrochloric acid, a precipitate of Prussian blue, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, will remain undissolved.

CHAPTER XXXIX.

FERRIC SALTS, Fe^{+++} . (FRESENIUS, p. 209.)

SOLUTIONS of ferric salts give no precipitate with hydrochloric acid. With *hydrogen sulphide* in acid solutions, they give a precipitate of sulphur, and the ferric salt is changed to a ferrous salt. Ammonium sulphide (or hydrogen sulphide in the presence of alkaline substances) produces a black precipitate of ferrous sulphide, FeS , mixed with sulphur.

Ammonium hydroxide added to solutions of ferric salts produces a reddish-brown precipitate of ferric hydroxide, $\text{Fe}(\text{OH})_3$, which is insoluble in an excess of the precipitant and in ammonium chloride solution. It is also insoluble in boiling sodium or potassium hydroxide solution, and in boiling sodium hypochlorite solution.

If an excess of *sodium acetate* is added to a nearly neutral solution of a ferric salt, and it is largely diluted and boiled, a precipitate of basic ferric acetate (a compound of the hydroxide and acetate) is produced. If this operation is performed in the presence of phosphate, oxalate, borate, or silicate radicals, these are precipitated in combination with the ferric radical.

If *potassium ferrocyanide* solution is added to an acid solution of a ferric salt, a precipitate of Prussian blue, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, is produced. An excess of the reagent is to be avoided, as the Prussian blue is slightly soluble in it.

If *ammonium thiocyanate* solution is added to an acid solution of a ferric salt, a blood-red solution containing ferric thiocyanate, $\text{Fe}(\text{CNS})_3$, is produced. The solution to which this test is applied should be cold, and large amounts of nitric acid should be avoided, as this decomposes the thiocyanate.

CHAPTER XL.

FERROUS SULFATE. MÄSENIUS, p. 106.

Ferrous salts are easily oxidized to ferric salts, converted into ferric salts by the action of oxidizing agents, especially by boiling nitric acid and hot aqueous solutions of potassium dichromate. The action of the oxygen of the air also effects the oxidation of ferrous salts.

Ferrous salts are reduced to ferric salts by the action of reducing agents, e.g. by hydrogen sulphide in acid solution, with the precipitation of sulphur, and by ammonium sulphide, with the precipitation of ferrous sulphide and sulphur.

In acid solutions, it reacts with potassium ferricyanide to produce a precipitate of Turnbull's blue, $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$.

CHAPTER XLI.

FLUORIDES, F'. (FRESENIUS, p. 339.)

MOST fluorides are decomposed by *concentrated sulphuric acid*, with the formation of hydrofluoric acid, HF. When this mixture of a decomposable fluoride and concentrated sulphuric acid is allowed to act upon glass (for instance, where marks are made through a coating of paraffin), the glass will be etched, on account of the formation of silicon fluoride, SiF_4 .

When a mixture of concentrated sulphuric acid with a decomposable fluoride, together with a silicate, is heated, silicon fluoride, SiF_4 , is evolved. If this gas is brought into contact with water by means of a current of dry air, silicic acid will be deposited, with the formation of hydrofluosilicic acid, H_2SiF_6 .

When heated in a bulb-tube with potassium disulphate or sodium metaphosphate, most fluorides evolve silicon fluoride, and this, coming into contact with water in the upper part of the tube, deposits silicic acid.

When a fluoride is mixed with its own weight of silica (if it does not already contain a sufficient quantity of that substance), the mixture fused with about 4 parts of sodium and potassium carbonates, the mass soaked out with water, and the solution filtered, the filtrate will contain all the fluorine. If this solution is now nearly neutralized with acetic acid, and an excess of calcium chloride solution is added, calcium fluoride, CaF_2 , will be precipitated along with calcium carbonate, silicate, etc. This precipitate may be collected upon a filter, dried, ignited, and tested for fluorine by the evolution of silicon fluoride.

CHAPTER XLII.

IODIDES, I'. (FRESENIUS, p. 361.)

BARIUM IODIDE and cadmium iodide are very soluble in water.

Neither hydriodic acid nor iodine is evolved upon boiling the solution of an iodide with acetic acid, even in the presence of chlorates and nitrates, provided that stronger acids are absent.

In neutral and acid solutions of iodides, *silver nitrate* produces a light yellow precipitate of silver iodide, AgI . This precipitate is insoluble in a mixture of 3 volumes of strong ammonium nitrate solution and 1 volume of ammonium hydroxide of .94 sp. gr.

When potassium dichromate and sulphuric or hydrochloric acid are added to the solution of an iodide, iodine is set free. If the experiment is performed in the presence of a little carbon disulphide, the latter assumes a beautiful violet color, on account of iodine dissolving in it. Sulphides and cyanides should be removed before this test is applied.

CHAPTER XLIII.

LEAD, Pb^{..}. (FRESENIUS, p. 232.)

IN rather concentrated solutions of lead salts, the addition of *hydrochloric acid* produces a partial precipitation of the lead as lead chloride, PbCl₂. The precipitate is soluble in boiling water.

Dilute *sulphuric acid* added in excess to a solution of lead chloride (or other lead salt) in water produces a precipitate of lead sulphate, PbSO₄.

In neutral or acid solutions of lead salts, *hydrogen sulphide* gives a black precipitate of lead sulphide, PbS. This is insoluble in yellow ammonium sulphide, but it dissolves in boiling, dilute nitric acid with the formation of lead nitrate, Pb(NO₃)₂, and the separation of sulphur.

When a solution of lead nitrate in nitric acid is evaporated with an excess of sulphuric acid, lead sulphate, PbSO₄, is produced, which does not dissolve in water containing dilute sulphuric acid.

CHAPTER XLIV.

LITHIUM, Li. (FRESENIUS, p. 144.)

LITHIUM CHLORIDE, sulphide, hydroxide, and carbonate are soluble in water (the latter rather sparingly), so that lithium is not precipitated by the group reagents. Under the conditions of the test for magnesium with sodium phosphate and ammonium hydroxide in *cold* solutions, lithium phosphate is not precipitated, although it would precipitate from such solutions, when not extremely dilute, if they were boiled.

Lithium sulphate may be converted into chloride by the addition of barium chloride to its solution. If barium hydroxide is added at the same time, lithium phosphate, oxalate, borate, etc., if present, cause the precipitation of the corresponding barium salts, and the lithium is obtained as chloride, after removing the excess of barium by means of ammonium carbonate, evaporating to dryness, and expelling ammonium salts by heating.

When a very concentrated solution of lithium chloride is boiled with an excess of *amyl alcohol* until the water has disappeared, and further until the amyl alcohol has become anhydrous, the lithium chloride dissolves in the amyl alcohol. Upon evaporating the solvent, the salt remains as a residue.

When introduced upon a clean platinum wire into the non-luminous gas flame, lithium salts, especially lithium chloride, impart to the flame a beautiful carmine-red color.

CHAPTER XLV.

MAGNESIUM, Mg^{++} . (FRESENIUS, p. 156.)

THE addition of hydrochloric acid to solutions of magnesium salts produces no precipitate, nor does the addition of hydrogen sulphide to acid solutions. In the presence of a sufficient amount of ammonium chloride, neither ammonium hydroxide, sulphide, nor carbonate gives a precipitate in solutions of magnesium salts which are soluble in water alone or in water containing ammonium chloride. When certain radicals are present, however, especially the phosphate or silicate radicals, the neutralization of an acid solution by ammonium hydroxide may precipitate ammonium magnesium phosphate, etc. The phosphate radical may be separated from magnesium by adding an excess of ferric chloride to the nearly neutral solution, and precipitating ferric phosphate along with basic ferric acetate by boiling the largely diluted solution with an excess of sodium acetate.

In solutions of magnesium salts, *sodium phosphate*, in the presence of ammonium salts, and especially in the presence of one third the total volume of ammonium hydroxide, produces a white, crystalline precipitate of ammonium magnesium phosphate, $NH_4MgPO_4 \cdot 6H_2O$.

In solutions of magnesium salts, when ammonium salts are absent, *barium hydroxide* gives a precipitate of magnesium hydroxide, $Mg(OH)_2$. The precipitation should be made in a hot solution, and a considerable excess of barium hydroxide should be used in order that the precipitation may be as complete as possible.

CHAPTER XLVI.

MANGANESE, Mn^{++} . (FRESENIUS, p. 194.)

IN solutions of manganese salts, neither hydrochloric acid nor hydrogen sulphide in the presence of acids produces precipitates. In the presence of ammonium salts, unless phosphates, etc., are present, ammonium hydroxide produces no precipitate in solutions of manganese salts, but the action of atmospheric oxygen upon such an ammoniacal solution gradually precipitates brown mangano-manganic oxide, $Mn_2O_3 \cdot xH_2O$.

Ammonium sulphide gives a flesh-colored or yellowish-white precipitate of manganese sulphide, $MnS \cdot H_2O$. This is readily soluble in a cold mixture of 1 volume of pure dilute hydrochloric acid and 3 volumes of hydrogen sulphide water.

In solutions of manganese salts, *sodium* or *potassium hydroxide* produces nearly white precipitates of manganese hydroxide, $Mn(OH)_2$, which is insoluble in an excess of the precipitant, and rapidly blackens upon exposure to the air, owing to the formation of higher oxides of manganese.

When a compound of manganese is fused with sodium carbonate and an oxidizing agent (*e.g.*, potassium nitrate or chlorate), or even with access of atmospheric air, a green mass is obtained, due to the presence of sodium manganate, Na_2MnO_4 .

CHAPTER XLVII.

MERCURIC SALTS, Hg^{++} . (FRESENIUS, p. 236.)

MERCURIC CHLORIDE is soluble in water, hence this salt does not form a precipitate.

In neutral or acid solutions of mercuric salts, *hydrogen sulphide* gives precipitates which may pass through white, yellow, and brown colors when the hydrogen sulphide is not in excess, on account of the formation of combinations of mercuric sulphide with the unchanged mercuric salt, *e.g.*, $2\text{HgS} \cdot \text{HgCl}_2$. With an excess of hydrogen sulphide, the precipitate is black mercuric sulphide, HgS . It is insoluble in ammonium sulphide. When washed free from hydrochloric acid and other chlorides (which with nitric acid produce aqua regia), mercuric sulphide is insoluble in boiling dilute nitric acid. If the boiling is continued for a long time, and especially if the nitric acid is concentrated, the mercuric sulphide is changed, without dissolving, into a white compound, $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$.

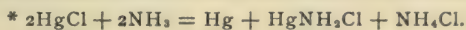
Mercuric sulphide dissolves in aqua regia with the formation of mercuric chloride, nitrate, or sulphate. A part of the sulphur usually separates in this operation.

When *stannous chloride* is added to the solution of a mercuric salt, a white precipitate of mercurous chloride is formed at first, and, if an excess of the reagent is used, a black precipitate of metallic mercury is finally produced.

CHAPTER XLVIII.

MERCUROUS SALTS, Hg⁺. (FRESENIUS, p. 229.)

WHEN added to a solution of a mercurous salt, hydrochloric acid yields a white precipitate of mercurous chloride, HgCl. The precipitate is insoluble in hot water. When treated with ammonium hydroxide, it gives a mixture of black metallic mercury and a light-colored compound, mercuric amido-chloride, HgNH₂Cl, which is invisible on account of the black mercury.* When treated with hot aqua regia, the black mixture is dissolved, with the formation of mercuric chloride, while any silver chloride that the substance may contain is undissolved, at least after dilution.



CHAPTER XLIX.

NICKEL, Ni⁺⁺. (FRESENIUS, p. 198.)

SOLUTIONS of nickel salts do not give precipitates with hydrochloric acid, with hydrogen sulphide in acid solutions, nor with ammonium hydroxide and ammonium chloride.

With *ammonium sulphide*, a black precipitate of nickel sulphide, NiS, is produced. The precipitate is practically insoluble in a cold mixture of 1 volume of pure dilute hydrochloric acid and 3 volumes of hydrogen sulphide water. It is best to wash the precipitate before treating it with this mixture, because, in the presence of nitrates, its solubility may be increased from the formation of aqua regia. Nickel sulphide dissolves readily in hot aqua regia, with the formation of chloride, nitrate, or sulphate, and usually with the separation of a part of the sulphur.

When a concentrated solution of a nickel salt containing but little free acid is treated with a little acetic acid, and a large excess of potassium nitrite is dissolved in it, no precipitate is produced, even after standing for several hours in a warm place.

In solutions of nickel salts, *sodium* or *potassium hydroxide* precipitates light green nickel hydroxide, $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$, which is insoluble in an excess of the precipitant.

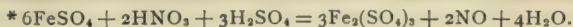
In the oxidizing flame, the *borax bead* is colored brownish-red when cold by compounds of nickel. This test cannot be applied in the presence of cobalt, on account of the much more powerful color produced by the latter.

CHAPTER L.

NITRATES, NO_3' . (FRESENIUS, p. 386.)

WITH the exception of a few basic salts, all nitrates are soluble in water.

If the solution of a nitrate is mixed with an equal volume of concentrated sulphuric acid, the mixture cooled, and a concentrated solution of *ferrous sulphate* added in a layer above the sulphuric acid solution, a brownish-black zone is formed at the junction of the two layers of liquid. The color is due to a compound of nitric oxide, NO ,* with ferrous sulphate. On account of their oxidizing action, chlorates interfere with this reaction. They may be decomposed by gently igniting the substance, mixed with sodium carbonate if necessary. This operation may change a nitrate to a nitrite, but the latter gives with sulphuric acid and ferrous sulphate the same reaction as a nitrate. Since iodides and bromides separate iodine and bromine when their solutions are mixed with concentrated sulphuric acid, they must be removed by precipitation with silver sulphate solution before the test for nitric acid is applied.



CHAPTER LI.

OXALATES, C_2O_4'' . (FRESENIUS, p. 337.)

OXALATES are decomposed by ignition, usually with the formation of carbonates, but sometimes with the formation of oxides or metals, where the carbonate is unstable or the oxide is readily reduced.

If a little *calcium chloride* is added to the dilute solution of an oxalate containing a little acetic acid, but no stronger free acid, a finely pulverulent, white precipitate of calcium oxalate, $CaC_2O_4 \cdot H_2O$ or $CaC_2O_4 \cdot 3H_2O$, is produced.

If a small quantity of *potassium permanganate* solution is added to a solution of an oxalate which is at about blood heat and acidified (best with sulphuric acid), the color of the permanganate disappears, and carbon dioxide is evolved. The identity of the carbon dioxide may be shown by passing it into calcium hydroxide solution. Many other reducing agents also decolorize potassium permanganate, but these do not evolve carbon dioxide, except in the case of formic acid and some other organic acids. Some reducing agents, like ferrous salts, may be oxidized without destroying the oxalic acid, by adding nitric acid and boiling. Solutions containing much hydrochloric acid decolorize permanganic acid, but in this case chlorine is liberated, and the latter does not effervesce as readily as carbon dioxide. Acid solutions of hydrogen peroxide also decolorize potassium permanganate solution, with effervescence, but in this case the escaping gas is oxygen.

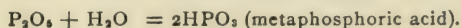
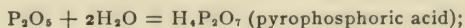
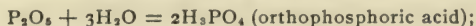
CHAPTER LII.

PHOSPHATES, PO_4''' .* (FRESENIUS, p. 327.)

MOST phosphates are soluble in nitric acid. The few native phosphates which do not dissolve in this acid are soluble in it after fusion with sodium carbonate, but this fusion does not always produce soluble sodium phosphate.

When the solution of a phosphate in nitric acid is added to an excess of *molybdic acid mixture*, and the liquid is gently warmed, a yellow precipitate of ammonium phosphomolybdate is produced. Its usual composition is represented by the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. Arsenates give an analogous precipitate, but this is not readily formed except on boiling. Arsenic acid, if present, should be removed by the use of hydrogen sulphide before the test for phosphoric acid is applied. The presence of hydrochloric acid and other chlorides interferes with the test, because the yellow precipitate is soluble in such solutions. Silicic acid also interferes with the reaction, since in its presence a yellow precipitate may be produced even in the absence of phosphoric acid. Hydro-

* Orthophosphates, corresponding to the acid H_3PO_4 , are to be understood when the term "phosphates" is used here. The salts corresponding to pyrophosphoric and metaphosphoric acids, $\text{H}_4\text{P}_2\text{O}_7$ and HPO_3 , are all converted into orthophosphates by fusion with sodium or potassium carbonate, or, if soluble, by boiling their solutions for a long time with acids. The derivation of the three kinds of phosphates from phosphoric anhydride and water may be shown by the following equations:



chloric acid may be removed to a sufficient extent, at least, and silicic acid rendered insoluble, by evaporating the solution to dryness with an excess of nitric acid, and taking up the residue with a little nitric acid and some water. It should be mentioned that, in the presence of tin, the operation just described may leave phosphoric acid undissolved in combination with stannic acid. Such a residue may be dissolved in hot ammonium sulphide, stannic sulphide precipitated by means of hydrochloric acid, and the filtrate tested as usual after the removal of hydrogen sulphide and chlorides by evaporation.

CHAPTER LIII.

POTASSIUM, K. (FRESENIUS, p. 131.)

POTASSIUM CHLORIDE, sulphide, hydroxide, carbonate, and phosphate being soluble in water, none of these compounds form precipitates in dilute aqueous solutions.

Potassium sulphate may be converted into potassium chloride by the addition of barium chloride to its solution. If barium hydroxide is added at the same time, potassium phosphate, oxalate, borate, etc., if present, cause the precipitation of the corresponding barium salts, and the potassium is obtained as chloride after removing the excess of barium by means of ammonium carbonate, evaporating to dryness, and expelling ammonium salts by heating.

Potassium chloride is not volatile below a red heat, but above that temperature it volatilizes with considerable rapidity.

When an excess of *amyl alcohol* is added to a very concentrated solution of potassium chloride and the mixture is boiled until the water has disappeared, and further until the amyl alcohol has become anhydrous, potassium chloride remains undissolved, and may be collected upon a filter which is free from water.

When *hydrochloroplatinic acid* is added to a *very* concentrated solution of a potassium salt, a yellow crystalline precipitate of potassium chloroplatinate, K_2PtCl_6 , is produced. Ammonium salts give a similar precipitate.

CHAPTER LIV.

SILICATES, SiO_4''' , SiO_3'' , etc. (FRESENIUS, p. 350.)

MANY of the natural silicates are not decomposed by acids (except hydrofluoric acid), but such silicates are decomposed by fusion with about four parts by weight of sodium and potassium carbonates. When the mass thus resulting is treated with water, and hydrochloric (or nitric) acid is added in excess to the solution and residue together, it usually happens that a part of the silicic acid precipitates, while some of it goes into solution with the chlorides (or nitrates) formed. When silicates that are decomposed by acids are treated with these solvents, it also usually happens that a part of the silicic acid goes into solution.

When a hydrochloric (or nitric) acid solution containing silicic acid is *evaporated to dryness*, and the residue is treated with hydrochloric (or nitric) acid, the silicic acid remains undissolved.

Upon fusing a fragment of a silicate in the sodium metaphosphate bead before the blowpipe, the silicic acid remains undissolved, forming a "skeleton" of the original fragment.

CHAPTER LV.

SILVER, Ag'. (FRESENIUS, p. 227.)

UPON the addition of *hydrochloric acid* to solutions of silver salts, a white curdy precipitate of silver chloride, AgCl, is produced. This precipitate blackens upon exposure to daylight. It is somewhat soluble in a large excess of hydrochloric acid, but is completely reprecipitated upon the addition of a sufficient amount of water. It does not dissolve in boiling water, but dissolves in dilute ammonium hydroxide solution, with the formation of compounds of silver chloride and ammonia, *e.g.*, $\text{AgCl} \cdot 2\text{NH}_3$. When this ammoniacal solution is acidified with nitric acid, silver chloride is reprecipitated.

CHAPTER LVI.

SODIUM, Na'. (FRESENIUS, p. 135.)

SODIUM CHLORIDE, sulphide, hydroxide, carbonate, and phosphate being soluble in water, none of these compounds form precipitates in dilute aqueous solutions.

Sodium sulphate may be converted into sodium chloride by the addition of barium chloride to its solution. If barium hydroxide is added at the same time, sodium phosphate, oxalate, borate, etc., if present, cause the precipitation of the corresponding barium salts, and the sodium is obtained as chloride, after removing the excess of barium by means of ammonium carbonate, evaporating to dryness, and expelling ammonium chloride by heating.

Sodium chloride is not volatile below a red heat, but above that temperature, it volatilizes with considerable rapidity.

When an excess of *amyl alcohol* is added to a very concentrated solution of sodium chloride, and the mixture is boiled until the water has disappeared, and further until the amyl alcohol has become anhydrous, sodium chloride remains undissolved, and may be collected on a filter which is free from water.

With hydrochloroplatinic acid, sodium salts give no precipitate, sodium chloroplatinate being very soluble in water.

Sodium salts give a very strong yellow color to the non-luminous flame. When this test is made, the platinum wire used for the purpose should be heated alone in the flame until it gives no yellow coloration, and nothing but an intense yellow flame should be taken as an indication of the presence of sodium.

CHAPTER LVII.

STANNIC SALTS, Sn^{++++} . (FRESENIUS, p. 268.)

SOLUTIONS of the ordinary stannic salts give no precipitate with hydrochloric acid, although certain solutions of metastannic acid may give one.

With *hydrogen sulphide*, acid solutions of stannic salts give a pale yellow precipitate of stannic sulphide, SnS_2 . This dissolves in yellow ammonium sulphide solution, forming ammonium thiostannate $(\text{NH}_4)_2\text{SnS}_3$. From the latter solution, hydrochloric acid, added to acid reaction, reprecipitates stannic sulphide.

Stannic sulphide dissolves in *boiling hydrochloric acid* (equal volumes of the concentrated acid and water), with the evolution of hydrogen sulphide and the formation of stannic chloride.

From solutions of stannic chloride, *metallic zinc* in contact with platinum foil precipitates metallic tin, partly upon the foil and partly as a spongy mass. The platinum foil is not blackened by this deposit.

Metallic tin dissolves in warm *hydrochloric acid*, with the evolution of hydrogen and the formation of stannous chloride.

When *mercuric chloride* is added to a solution of stannous chloride, a white precipitate of mercurous chloride is produced if the mercuric chloride is in excess, but if the stannous chloride is in excess, black metallic mercury is formed.

CHAPTER LVIII.

STANNOUS SALTS, Sn^{++} . (FRESENIUS, p. 264.)

SOLUTIONS of stannous salts give no precipitates with hydrochloric acid.

With *hydrogen sulphide*, acid solutions give a brownish-black precipitate of stannous sulphide, SnS . This precipitate dissolves in yellow ammonium sulphide, if enough extra sulphur is present, forming ammonium thiostannate, $(\text{NH}_4)_2\text{SnS}_3$. From the latter solution, an excess of hydrochloric acid will precipitate *stannic* sulphide, SnS_2 . The behavior of *stannic* sulphide is described in the preceding chapter.

CHAPTER LIX.

STRONTIUM, Sr. (FRESENIUS, p. 150.)

STRONTIUM CHLORIDE, sulphide, and hydroxide are soluble in water, hence they cannot form precipitates in dilute aqueous solutions.

Strontium phosphate, oxalate, borate, and silicate are soluble in hydrochloric or nitric acid, but they are insoluble or in some cases nearly insoluble in water in the presence of neutral or alkaline compounds. Upon neutralizing an acid solution, ammonium hydroxide may therefore precipitate these strontium salts, if the radicals which form them are present. When strontium phosphate, oxalate, borate, or silicate is dissolved in hydrochloric acid, an excess of ferric chloride added, the solution neutralized with sodium carbonate as far as possible without producing a permanent precipitate, an excess of sodium acetate added, and the liquid largely diluted and then boiled, ferric phosphate, oxalate, borate, or silicate is precipitated, together with basic ferric acetate, while the strontium remains in solution.

Ammonium carbonate added to solutions of strontium salts gives a precipitate of strontium carbonate, SrCO_3 . The presence of ammonium hydroxide aids this precipitation by its tendency to prevent the formation of soluble acid strontium carbonate, $\text{Sr}(\text{HCO}_3)_2$.

Strontium carbonate dissolves in hydrochloric acid and in nitric acid, with the formation of strontium chloride and nitrate. Upon evaporating the solutions, the solid salts are obtained.

Potassium dichromate produces no precipitate when added with sodium acetate to the neutral solution of a strontium salt. From such a solution, made alkaline with ammonium hydroxide and containing a strontium salt and chromate, ammonium carbonate precipitates strontium carbonate.

When a very concentrated solution of strontium nitrate is boiled with an excess of *amyl alcohol* until the water has disappeared, and further until the amyl alcohol has become anhydrous, the strontium nitrate is precipitated, and may be collected upon a filter which is free from water.

When strontium nitrate is introduced into a non-luminous *gas flame*, it imparts to the latter an intense red color.

When *potassium sulphate* solution is added to the solution of a strontium salt, a white precipitate of strontium sulphate, SrSO_4 , is formed.

CHAPTER LX.

SULPHATES, SO_4'' . (FRESENIUS, p. 324.)

DILUTE solutions of sulphates give no precipitates with silver nitrate solution.

Solutions of sulphates acidified with hydrochloric (or nitric) acid, with *barium chloride* (or *nitrate*) solution, give white precipitates of barium sulphate, BaSO_4 .

When a sulphate which is insoluble in acids (for example, barium sulphate) is fused with about four parts of sodium carbonate, and the resulting mass is treated with water, sodium sulphate goes into solution along with the excess of sodium carbonate.

When a sulphate is fused with sodium carbonate before the blowpipe on charcoal, sodium sulphide, Na_2S , is produced, and if the part of the charcoal into which the mass has penetrated is placed with a few drops of water upon a bright silver surface, the latter is blackened. This reaction is produced by all compounds containing sulphur.

CHAPTER LXI.

SULPHIDES, S". (FRESENIUS, p. 372.)

A NUMBER of sulphides dissolve in hydrochloric or sulphuric acid, with the evolution of hydrogen sulphide, and the latter is readily detected by the fact that it blackens paper which has been moistened with an alkaline lead solution. Nearly all of them dissolve in hot nitric acid, with the evolution of red fumes and separation of sulphur. By powerful oxidizing agents, both in the wet and the dry way, sulphides are converted into sulphates.

When *cadmium sulphate* solution is added to the solution of a sulphide, a yellow precipitate of cadmium sulphide, CdS , is formed, either in neutral, alkaline, or acid solutions. By adding an excess of this reagent, and filtering, the sulphide radical may be completely removed from a solution.

CHAPTER LXII.

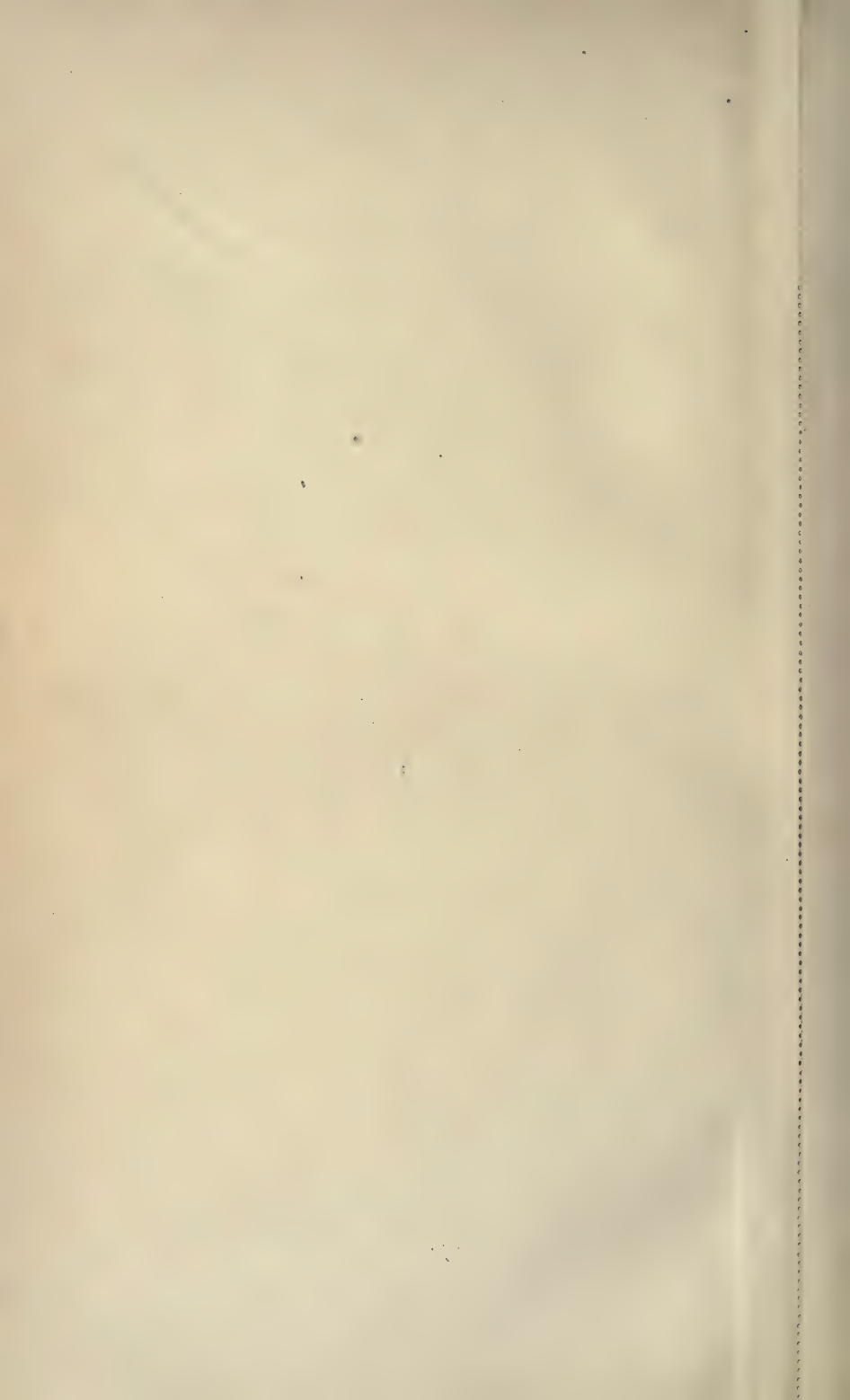
ZINC, Zn^{++} . (FRESENIUS, p. 190.)

HYDROCHLORIC ACID produces no precipitates in solutions of zinc salts, nor does hydrogen sulphide produce a precipitate in solutions containing a considerable amount of a strong acid, *i.e.*, hydrochloric, sulphuric, or nitric acid.

When ammonium hydroxide is added in excess to a solution of a zinc salt, any precipitate that may form at the point of neutrality is redissolved, and a clear solution results.

In solutions of zinc salts, *ammonium sulphide* produces a white precipitate of zinc sulphide, ZnS . This dissolves in a mixture of 1 volume of pure dilute hydrochloric acid and 3 volumes of hydrogen sulphide water, with the formation of zinc chloride.

In solutions of zinc salts, sodium or potassium hydroxide added in excess redissolves the precipitate produced at the point of neutrality, and a clear solution results if heat is not applied. (Boiling reprecipitates a large part of the zinc hydroxide if the excess of sodium or potassium hydroxide is not too great.)



APPENDIX I.

LIST OF APPARATUS.

THE following list of apparatus may be supplied to each student beginning the course in qualitative analysis. New supplies will be needed from time to time as material is broken or used.

- 2 nests of lipped beakers, low form, 1-6.
- 2 " " " " " " 1-4.
- 1 graduated cylinder, 100 cc.
- 4 flasks, vial mouth, flat bottom, 250 cc (8 oz.).
- 1 flask, ring neck, flat bottom, 1000 cc (32 oz.), for wash-bottle.
- 1 distilling-flask, 250 cc (8 oz.).
- 4 funnels, $2\frac{1}{2}$ in. diam.
- 4 " 3 " "
- 2 doz. test-tubes, $\frac{3}{4} \times 6$ in.
- $\frac{1}{2}$ lb. glass tubing and rods.
- 4 watch-glasses, 2 in.
- Reagent bottles.*
- 4 casseroles, Royal Berlin, No. 3A.
- 1 mortar and pestle, 4 in.
- 4 crucibles, Royal Berlin, No. 00, without covers.
- 2 packages round filters, 11 cm.
- 2 " " " " $12\frac{1}{2}$ cm.

* About 15 bottles for the more frequently used reagents may be supplied to each student, including a bottle for silver nitrate, and a small one for about 10 cc of hydrochloroplatinic acid (5 per cent platinum solution).

- 1 box folded filters, 12 cm.
- 1 rubber stopper, 2 holes, for wash-bottle.
- 2 ft. rubber tubing, $\frac{1}{4}$ in., for Bunsen burner.
- 1 ft. " " $\frac{3}{16}$ in.
- 1 Bunsen burner.
- 1 triangular file.
- 1 lamp-stand, with rings.
- 1 platinum foil, 1×2 in.
- $\frac{1}{2}$ ft. platinum wire, small.
- 1 pair pliers.
- 1 iron triangle for porcelain crucibles.
- 1 piece wire gauze, iron, 5×5 in.
- Filter-stands of wood, for several funnels.
- 1 box gummed labels.
- 1 horn spatula.
- Matches.
- 1 coarse sponge.
- 1 test-tube holder.
- 1 test-tube rack.
- Towels.
- Note-book.
- Apron.

APPENDIX II.

LABELS FOR EXPERIMENTAL SOLUTIONS.

METALLIC RADICALS.

Al^{\cdots}

ALUMINIUM

$\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ in 50 parts H_2O

NH_4^{\cdot}

AMMONIUM

NH_4Cl in 20 parts H_2O

Sb^{\cdots}

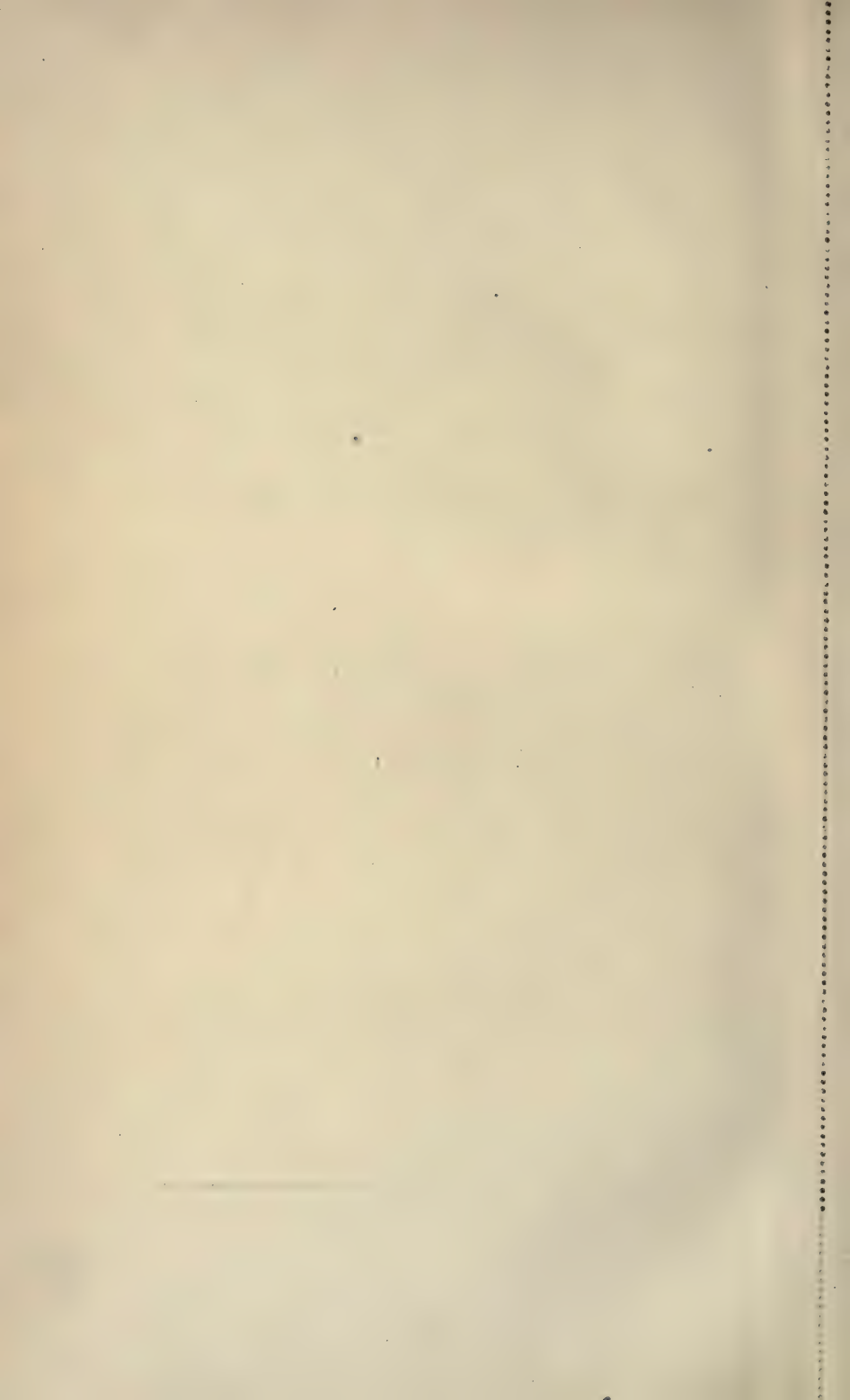
ANTIMONIOUS

SbCl_3 (with HCl) in 50 parts H_2O

As^{\cdots}

ARSENIOUS

AsCl_3 (As_2O_3 in HCl) in 50 parts H_2O



Ba^{..}

BARIUM

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 20 parts H_2O

Bi^{...}

BISMUTH

$\text{Bi}(\text{NO}_3)_3$ (with HNO_3) in 50 parts H_2O

Cd^{..}

CADMIUM

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 50 parts H_2O

Ca^{..}

CALCIUM

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 parts H_2O

Cr^{...}

CHROMIUM

$\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ in 50 parts H_2O

Co^{..}

COBALT

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 50 parts H_2O

Cu^{..}

CUPRIC

Cu(NO₃)₂ in 50 parts H₂O

Fe^{...}

FERRIC

FeCl₃.?H₂O in 50 parts H₂O

Fe^{..}

FERROUS

FeSO₄.7H₂O in 50 parts H₂O

Pb^{..}

LEAD

Pb(NO₃)₂ in 20 parts H₂O

Li[.]

LITHIUM

LiCl in 20 parts H₂O

Mg^{..}

MAGNESIUM

MgCl₂.6H₂O in 20 parts H₂O

Mn^{..}

MANGANESE

MnCl₂·4H₂O in 50 parts H₂O

Hg^{..}

MERCURIC

HgCl₂ in 50 parts H₂O

Hg[·]

MERCUROUS

HgNO₂ (with HNO₃) in 50 parts H₂O

Ni^{..}

NICKEL

NiCl₂·6H₂O in 50 parts H₂O

K[·]

POTASSIUM

KCl in 20 parts H₂O

Na[·]

SODIUM

NaCl in 20 parts H₂O

Ag[·]

SILVER

AgNO₃ in 50 parts H₂O

Sn^{···}

STANNIC

SnCl₄ (or SnBr₄) in 50 parts H₂O

Sn^{··}

STANNOUS

SnCl₂.2H₂O in 50 parts H₂O

Sr^{··}

STRONTIUM

SrCl₂.6H₂O in 20 parts H₂O

Zn^{··}

ZINC

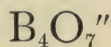
ZnSO₄.7H₂O in 50 parts H₂O

ACID RADICALS.



ARSENATE

$\text{HNa}_2\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ in 20 parts H_2O



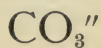
BORATE

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in 20 parts H_2O



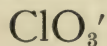
BROMIDE

KBr in 100 parts H_2O



CARBONATE

Na_2CO_3 in 20 parts H_2O



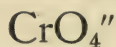
CHLORATE

KClO_3 in 20 parts H_2O



CHLORIDE

NaCl in 100 parts H_2O



CHROMATE

K_2CrO_4 in 20 parts H_2O



CYANIDE

KCN in 20 parts H_2O



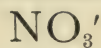
FLUORIDE

NaF in 100 parts H_2O



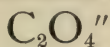
IODIDE

KI in 100 parts H_2O



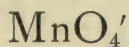
NITRATE

KNO_3 in 20 parts H_2O



OXALATE

$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in 25 parts H_2O



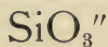
PERMANGANATE

KMnO_4 in 100 parts H_2O



PHOSPHATE

$\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in 20 parts H_2O



SILICATE

$\text{Na}_4\text{SiO}_4(?)$ in 100 parts H_2O



SULPHATE

K_2SO_4 in 20 parts H_2O



SULPHIDE

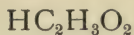
$(\text{NH}_4)_2\text{S}$, Dilute solution.

APPENDIX III.

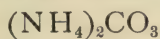
LABELS FOR REAGENTS.

LIQUIDS.

ACETIC ACID



AMMONIUM CARBONATE



AMMONIUM CHLORIDE



AMMONIUM HYDROXIDE

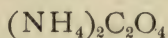


Dilute

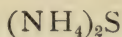
1 volume NH_4OH , .94 sp. gr.

3 volumes NH_4NO_3 solution

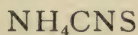
AMMONIUM OXALATE



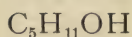
AMMONIUM SULPHIDE



AMMONIUM THIOCYANATE



AMYL ALCOHOL



BARIUM CHLORIDE



BARIUM HYDROXIDE



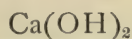
CADMIUM SULPHATE



CALCIUM CHLORIDE



CALCIUM HYDROXIDE



CARBON DISULPHIDE



CHLORINE WATER



ETHYL ALCOHOL



FERRIC CHLORIDE



FERROUS SULPHATE



Saturated solution

HYDROCHLORIC ACID



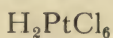
Dilute

HYDROCHLORIC ACID



Concentrated

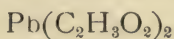
HYDROCHLOROPLATINIC ACID



HYDROGEN SULPHIDE WATER



LEAD ACETATE



MERCURIC CHLORIDE



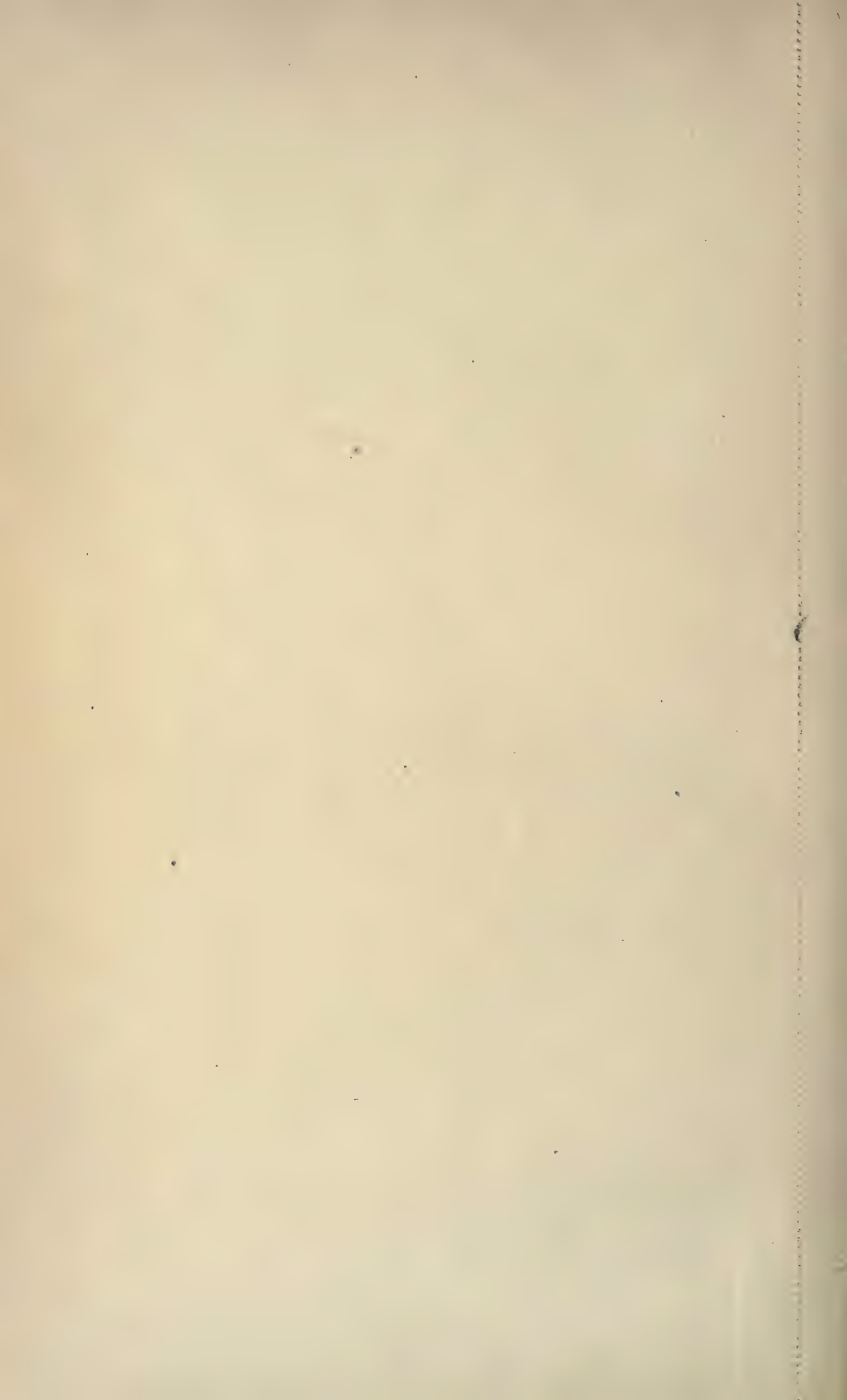
MOLYBDIC ACID MIXTURE



NITRIC ACID



Dilute



NITRIC ACID

HNO_3
Concentrated

POTASSIUM DICHROMATE

$\text{K}_2\text{Cr}_2\text{O}_7$

POTASSIUM FERROCYANIDE

$\text{K}_4\text{Fe}(\text{CN})_6$

POTASSIUM HYDROXIDE

KOH

POTASSIUM PERMANGANATE

KMnO_4

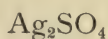
POTASSIUM SULPHATE

K_2SO_4

SILVER NITRATE

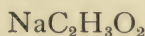
AgNO_3

SILVER SULPHATE

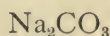


In dilute H_2SO_4

SODIUM ACETATE



SODIUM CARBONATE



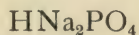
SODIUM HYDROXIDE



SODIUM HYPOCHLORITE



SODIUM PHOSPHATE



SODIUM SULPHIDE



STANNOUS CHLORIDE



SULPHURIC ACID



Dilute

SULPHURIC ACID



Concentrated

SOLIDS.

BARIUM SULPHATE

BaSO_4

CALCIUM FLUORIDE

CaF_2

CALCIUM HYDROXIDE

$(\text{CaOH})_2$

FERROUS SULPHATE

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

PARAFFIN

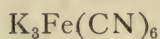
POTASSIUM CHLORATE

KClO_3

POTASSIUM CYANIDE

KCN

POTASSIUM FERRICYANIDE



POTASSIUM IODIDE



POTASSIUM NITRATE

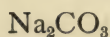


POTASSIUM NITRITE

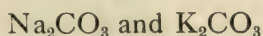


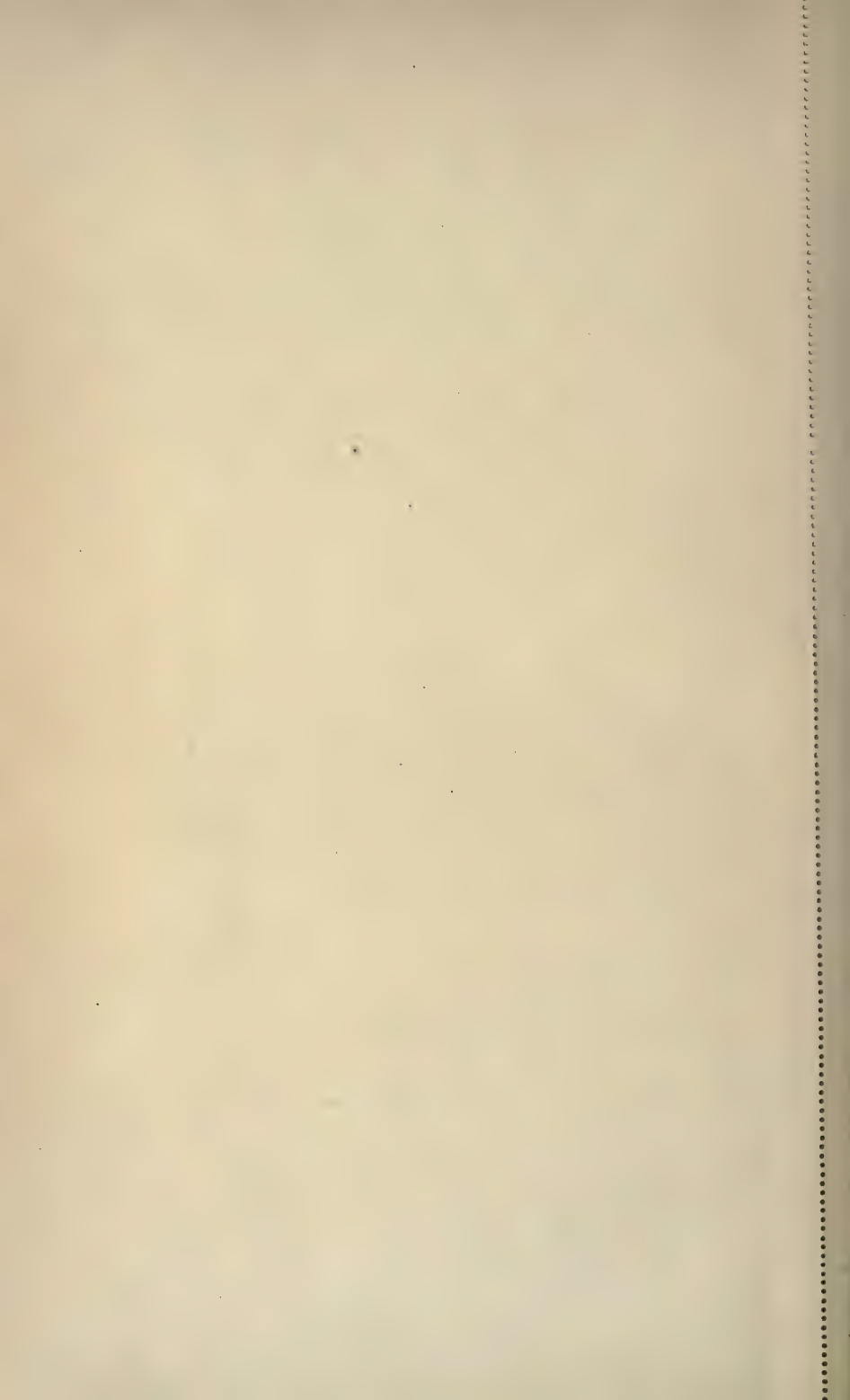
POWDERED GLASS

SODIUM CARBONATE

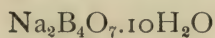


SODIUM AND POTASSIUM CARBONATES





SODIUM TETRABORATE



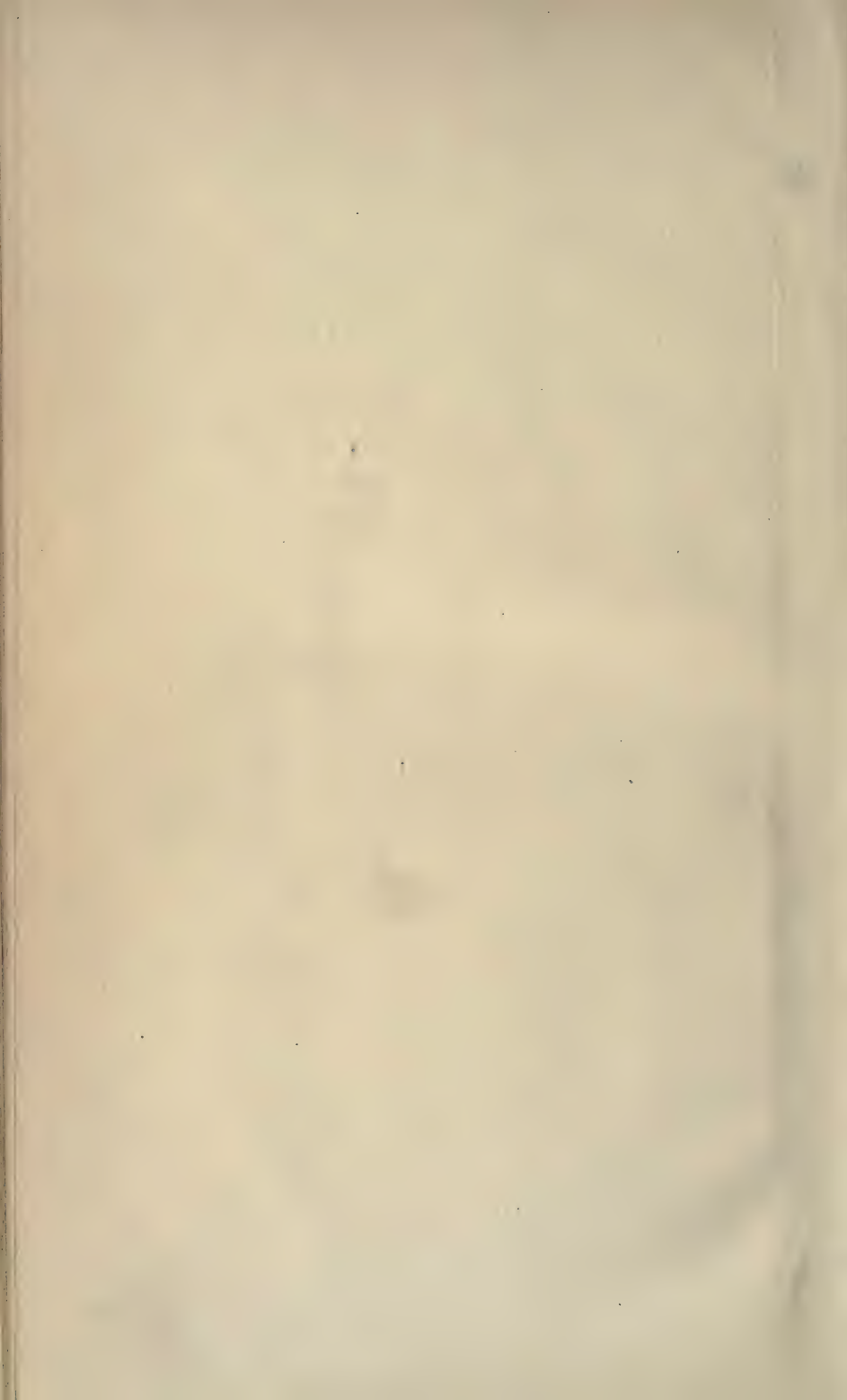
TARTARIC ACID



TEST PAPERS

ZINC





SHORT-TITLE CATALOGUE

OF THE

PUBLICATIONS

OF

JOHN WILEY & SONS,

NEW YORK.

LONDON: CHAPMAN & HALL, LIMITED.

ARRANGED UNDER SUBJECTS.

Descriptive circulars sent on application.

Books marked with an asterisk are sold at *net* prices only.

All books are bound in cloth unless otherwise stated.

AGRICULTURE.

Armsby's Manual of Cattle Feeding.....	12mo,	\$1 75
Downing's Fruit and Fruit Trees.....	8vo,	5 00
Grotenfelt's The Principles of Modern Dairy Practice. (Woll.)		
	12mo,	2 00
Kemp's Landscape Gardening.....	12mo,	2 50
Maynard's Landscape Gardening.....	12mo,	1 50
Steel's Treatise on the Diseases of the Dog.....	8vo,	3 50
Stockbridge's Rocks and Soils.....	8vo,	2 50
Woll's Handbook for Farmers and Dairymen.....	12mo,	1 50

ARCHITECTURE.

Berg's Buildings and Structures of American Railroads.....	4to,	5 00
Birkmire's American Theatres—Planning and Construction.....	8vo,	3 00
“ Architectural Iron and Steel.....	8vo,	3 50
“ Compound Riveted Girders.....	8vo,	2 00
“ Skeleton Construction in Buildings.....	8vo,	3 00
“ Planning and Construction of High Office Buildings.		
	8vo,	3 50
Briggs' Modern Am. School Building.....	8vo,	4 00
Carpenter's Heating and Ventilating of Buildings.....	8vo,	3 00

Freitag's Architectural Engineering....	8vo,	\$2 50
“ The Fireproofing of Steel Buildings	8vo,	2 50
Gerhard's Sanitary House Inspection.....	16mo,	1 00
“ Theatre Fires and Panics.....	12mo,	1 50
Hatfield's American House Carpenter.....	8vo,	5 00
Holly's Carpenter and Joiner.....	18mo,	75
Kidder's Architect and Builder's Pocket-book...16mo, morocco,		4 00
Merrill's Stones for Building and Decoration.....	8vo,	5 00
Monckton's Stair Building—Wood, Iron, and Stone.....	4to,	4 00
Wait's Engineering and Architectural Jurisprudence.....	8vo,	6 00
	Sheep,	6 50
“ Law of Operations Preliminary to Construction in En- gineering and Architecture.....	8vo,	5 00
	Sheep,	5 50
Worcester's Small Hospitals—Establishment and Maintenance, including Atkinson's Suggestions for Hospital Archi- tecture....	12mo,	1 25
* World's Columbian Exposition of 1893.....	Large 4to,	1 00

ARMY, NAVY, Etc.

Bernadou's Smokeless Powder.....	12mo,	2 50
* Bruff's Ordnance and Gunnery.....	8vo,	6 00
Chase's Screw Propellers.....	8vo,	3 00
Cronkhite's Gunnery for Non-com. Officers.....	32mo, morocco,	2 00
* Davis's Treatise on Military Law.....	8vo,	7 00
	Sheep,	7 50
* “ Elements of Law.....	8vo,	2 50
De Brack's Cavalry Outpost Duties. (Carr.)....	32mo, morocco,	2 00
Dietz's Soldier's First Aid.....	16mo, morocco,	1 25
* Dredge's Modern French Artillery....	Large 4to, half morocco,	15 00
* “ Record of the Transportation Exhibits Building, World's Columbian Exposition of 1893..	4to, half morocco,	5 00
Durand's Resistance and Propulsion of Ships.....	8vo,	5 00
* Fiebigger's Field Fortification, including Military Bridges, Demolitions, Encampments and Communications.		
	Large 12mo,	2 00
* Dyer's Light Artillery.....	12mo,	3 00
* Hoff's Naval Tactics.....	8vo,	1 50
* Ingalls's Ballistic Tables.....	8vo,	1 50

Ingalls's Handbook of Problems in Direct Fire.....	8vo,	\$4 00
Mahan's Permanent Fortifications. (Mercur.).....	8vo, half morocco,	7 50
Manual for Courts-Martial.....	16mo, morocco,	1 50
* Mercur's Attack of Fortified Places.....	12mo,	2 00
* " Elements of the Art of War.....	8vo,	4 00
Metcalf's Ordnance and Gunnery.....	12mo, with Atlas,	5 00
Murray's Infantry Drill Regulations adapted to the Springfield Rifle, Caliber .45.....	32mo, paper,	10
* Phelps's Practical Marine Surveying.....	8vo,	2 50
Powell's Army Officer's Examiner.....	12mo,	4 00
Sharpe's Subsisting Armies.....	32mo, morocco,	1 50
Wheeler's Siege Operations.....	8vo,	2 00
Winthrop's Abridgment of Military Law.....	12mo,	2 50
Woodhull's Notes on Military Hygiene.....	16mo,	1 50
Young's Simple Elements of Navigation.....	16mo, morocco,	2 00
" " " " " first edition.....		1 00

ASSAYING.

Fletcher's Quant. Assaying with the Blowpipe.....	16mo, morocco,	1 50
Furman's Practical Assaying.....	8vo,	3 00
Kunhardt's Ore Dressing.....	8vo,	1 50
Miller's Manual of Assaying.....	12mo,	1 00
O'Driscoll's Treatment of Gold Ores.....	8vo,	2 00
Ricketts and Miller's Notes on Assaying.....	8vo,	3 00
Thurston's Alloys, Brasses, and Bronzes.....	8vo,	2 50
Wilson's Cyanide Processes.....	12mo,	1 50
" The Chlorination Process.....	12mo,	1 50

ASTRONOMY.

Craig's Azimuth.....	4to,	3 50
Doolittle's Practical Astronomy.....	8vo,	4 00
Gore's Elements of Geodesy.....	8vo,	2 50
Hayford's Text-book of Geodetic Astronomy.....	8vo,	3 00
* Michie and Harlow's Practical Astronomy.....	8vo,	3 00
* White's Theoretical and Descriptive Astronomy.....	12mo,	2 00

BOTANY.

Baldwin's Orchids of New England.....	Small 8vo,	1 50
Thomé's Structural Botany.....	16mo,	2 25
Westermaier's General Botany. (Schneider.).....	8vo,	2 00

BRIDGES, ROOFS, Etc.

(See also ENGINEERING, p. 7.)

Boller's Highway Bridges.....	8vo,	\$2 00
* " The Thames River Bridge.....	4to, paper,	5 00
Burr's Stresses in Bridges.....	8vo,	3 50
Crehore's Mechanics of the Girder.....	8vo,	5 00
Du Bois's Stresses in Framed Structures.....	Small 4to,	10 00
Foster's Wooden Trestle Bridges.....	4to,	5 00
Greene's Arches in Wood, etc.....	8vo,	2 50
" Bridge Trusses.....	8vo,	2 50
" Roof Trusses.....	8vo,	1 25
Howe's Treatise on Arches.....	8vo,	4 00
Johnson's Modern Framed Structures.....	Small 4to,	10 00
Merriman & Jacoby's Text-book of Roofs and Bridges.		
Part I., Stresses.....	8vo,	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges.		
Part II., Graphic Statics.....	8vo,	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges.		
Part III., Bridge Design.....	8vo,	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges.		
Part IV., Continuous, Draw, Cantilever, Suspension, and		
Arched Bridges.....	8vo,	2 50
* Morison's The Memphis Bridge.....	Oblong 4to,	10 00
Waddell's De Pontibus (a Pocket-book for Bridge Engineers).		
	16mo, morocco,	3 00
" Specifications for Steel Bridges.....	12mo,	1 25
Wood's Construction of Bridges and Roofs.....	8vo,	2 00
Wright's Designing of Draw Spans. Parts I. and II.....	8vo, each	2 50
" " " " " Complete.....	8vo,	3 50

CHEMISTRY—BIOLOGY—PHARMACY—SANITARY SCIENCE.

Adriance's Laboratory Calculations.....	12mo,	1 25
Allen's Tables for Iron Analysis.....	8vo,	3 00
Austen's Notes for Chemical Students.....	12mo,	1 50
Bolton's Student's Guide in Quantitative Analysis.....	8vo,	1 50
Classen's Analysis by Electrolysis. (Herrick and Boltwood.).....	8vo,	3 00

Cohn's Indicators and Test-papers.....	12mo	\$2 00
Crafts's Qualitative Analysis. (Schaeffer.).....	12mo,	1 50
Davenport's Statistical Methods with Special Reference to Bio- logical Variations	12mo, morocco,	1 25
Drechsel's Chemical Reactions. (Merrill.).....	12mo,	1 25
Erdmann's Introduction to Chemical Preparations. (Dunlap.) 12mo,		1 25
Fresenius's Quantitative Chemical Analysis. (Allen.).....	8vo,	6 00
" Qualitative " " (Johnson.).....	8vo,	3 00
" " " " (Wells.) Trans.		
16th German Edition.....	8vo,	5 00
Fuertes's Water and Public Health.....	12mo,	1 50
" Water Filtration Works.....	12mo,	2 50
Gill's Gas and Fuel Analysis.....	12mo,	1 25
Goodrich's Economic Disposal of Towns' Refuse.....	Demy 8vo,	3 50
Hammarsten's Physiological Chemistry. (Mandel.).....	8vo,	4 00
Helm's Principles of Mathematical Chemistry. (Morgan.)	12mo,	1 50
Hopkins' Oil-Chemist's Hand-book.....	8vo,	3 00
Ladd's Quantitative Chemical Analysis.....	12mo,	1 00
Landauer's Spectrum Analysis. (Tingle.).....	8vo,	3 00
Löb's Electrolysis and Electrosynthesis of Organic Compounds. (Lorenz.).....	12mo,	1 00
Mandel's Bio-chemical Laboratory.....	12mo,	1 50
Mason's Water-supply.....	8vo,	5 00
" Examination of Water.....	12mo,	1 25
Meyer's Radicles in Carbon Compounds. (Tingle.).....	12mo,	1 00
Mixer's Elementary Text-book of Chemistry.....	12mo,	1 50
Morgan's The Theory of Solutions and its Results.....	12mo,	1 00
" Elements of Physical Chemistry.....	12mo,	2 00
Nichols's Water-supply (Chemical and Sanitary).....	8vo,	2 50
O'Brine's Laboratory Guide to Chemical Analysis.....	8vo,	2 00
Pinner's Organic Chemistry. (Austen.).....	12mo,	1 50
Poole's Calorific Power of Fuels.....	8vo,	3 00
Richards's Cost of Living as Modified by Sanitary Science..	12mo.	1 00
" and Woodman's Air, Water, and Food.....	8vo,	2 00
Ricketts and Russell's Notes on Inorganic Chemistry (Non- metallic).....	Oblong 8vo, morocco,	75
Rideal's Sewage and the Bacterial Purification of Sewage..	8vo,	3 50
Ruddiman's Incompatibilities in Prescriptions.....	8vo,	2 00
Schimpf's Volumetric Analysis.....	12mo,	2 50
Spencer's Sugar Manufacturer's Handbook.....	16mo, morocco,	2 00
" Handbook for Chemists of Beet Sugar Houses. 16mo, morocco,		3 00
Stockbridge's Rocks and Soils.....	8vo,	2 50
* Tillman's Descriptive General Chemistry.....	8vo,	3 00

Van Deventer's Physical Chemistry for Beginners. (Boltwood.)	12mo,	\$1 50
Wells's Inorganic Qualitative Analysis.....	12mo,	1 50
" Laboratory Guide in Qualitative Chemical Analysis.	8vo,	1 50
Whipple's Microscopy of Drinking-water.....	8vo,	3 50
Wiechmann's Chemical Lecture Notes.....	12mo,	3 00
" Sugar Analysis.....	Small 8vo,	2 50
Wulling's Inorganic Phar. and Med. Chemistry.....	12mo,	2 00

DRAWING.

* Bartlett's Mechanical Drawing.....	8vo,	3 00
Hill's Shades and Shadows and Perspective.....	8vo,	2 00
MacCord's Descriptive Geometry.....	8vo,	3 00
" Kinematics.....	8vo,	5 00
" Mechanical Drawing.....	8vo,	4 00
Mahan's Industrial Drawing. (Thompson.).....	2 vols., 8vo,	3 50
Reed's Topographical Drawing. (H. A.).....	4to,	5 00
Reid's A Course in Mechanical Drawing.....	8vo.	2 00
" Mechanical Drawing and Elementary Machine Design.	8vo,	3 00
Smith's Topographical Drawing. (Macmillan.).....	8vo,	2 50
Warren's Descriptive Geometry.....	2 vols., 8vo,	3 50
" Drafting Instruments.....	12mo,	1 25
" Free-hand Drawing.....	12mo,	1 00
" Linear Perspective.....	12mo,	1 00
" Machine Construction.....	2 vols., 8vo,	7 50
" Plane Problems.....	12mo,	1 25
" Primary Geometry.....	12mo,	75
" Problems and Theorems.....	8vo,	2 50
" Projection Drawing.....	12mo,	1 50
" Shades and Shadows.....	8vo,	3 00
" Stereotomy—Stone-cutting.....	8vo,	2 50
Whelpley's Letter Engraving.....	12mo,	2 00
Wilson's Free-hand Perspective.....	8vo,	2 50

ELECTRICITY, MAGNETISM, AND PHYSICS.

Anthony and Brackett's Text-book of Physics. (Magie.) Small	8vo,	3 00
Anthony's Theory of Electrical Measurements.....	12mo,	1 00
Barker's Deep-sea Soundings.....	8vo,	2 00
Benjamin's Voltaic Cell.....	8vo,	3 00
" History of Electricity.....	8vo,	3 00

Classen's Analysis by Electrolysis. (Herrick and Boltwood.)	8vo,	\$3 00
Crehore and Squier's Experiments with a New Polarizing Photo- Chronograph.....	8vo,	3 00
Dawson's Electric Railways and Tramways. Small, 4to, half morocco,	12 50	
* "Engineering" and Electric Traction Pocket-book. 16mo, morocco,	5 00	
* Dredge's Electric Illuminations.... 2 vols., 4to, half morocco,	25 00	
" " " Vol. II.....	4to,	7 50
Gilbert's De magnete. (Mottelay).....	8vo,	2 50
Holman's Precision of Measurements.....	8vo,	2 00
" Telescope-mirror-scale Method.....	Large 8vo,	75
Le Chatelier's High Temperatures. (Burgess).....	12mo,	3 00
Löb's Electrolysis and Electrosynthesis of Organic Compounds. (Lorenz.).....	12mo,	1 00
Lyons's Electromagnetic Phenomena and the Deviations of the Compass.....	8vo,	6 00
* Michie's Wave Motion Relating to Sound and Light.....	8vo,	4 00
Morgan's The Theory of Solutions and its Results.....	12mo,	1 00
Niaudet's Electric Batteries (Fishback.).....	12mo,	2 50
* Parshall & Hobart Electric Generators. Small 4to, half mor.,	10 00	
Pratt and Alden's Street-railway Road-beds.....	8vo,	2 00
Reagan's Steam and Electric Locomotives.....	12mo,	2 00
Thurston's Stationary Steam Engines for Electric Lighting Pur- poses.....	8vo,	2 50
* Tillman's Heat.....	8vo,	1 50
Tory & Pitcher's Laboratory Physics.....	Small 8vo,	2 00

ENGINEERING.

CIVIL—MECHANICAL—SANITARY, ETC.

See also BRIDGES, p. 4; HYDRAULICS, p. 9; MATERIALS OF EN-
GINEERING, p. 11; MECHANICS AND MACHINERY, p. 12; STEAM
ENGINES AND BOILERS, p. 14.)

Baker's Masonry Construction.....	8vo,	5 00
" Surveying Instruments.....	12mo,	3 00
Black's U. S. Public Works.....	Oblong 4to,	5 00
Brooks's Street-railway Location.....	16mo, morocco,	1 50
Butts's Civil Engineers' Field Book.....	16mo, morocco,	2 50
Byrne's Highway Construction.....	8vo,	5 00
" Inspection of Materials and Workmanship.....	16mo,	3 00
Carpenter's Experimental Engineering.....	8vo,	6 00
Church's Mechanics of Engineering—Solids and Fluids....	8vo,	6 00

Church's Notes and Examples in Mechanics	8vo,	\$2 00
Crandall's Earthwork Tables	8vo,	1 50
" The Transition Curve	16mo, morocco,	1 50
Davis's Elevation and Stadia Tables	Small 8vo,	1 00
Dredge's Penn. Railroad Construction, etc. Large 4to,		
half morocco, \$10; paper,		5 00
* Drinker's Tunnelling	4to, half morocco,	25 00
Eissler's Explosives—Nitroglycerine and Dynamite	8vo,	4 00
Frizell's Water Power	8vo,	5 00
Folwell's Sewerage	8vo,	3 00
" Water-supply Engineering	8vo,	4 00
Fowler's Coffe-dam Process for Piers	8vo.	2 50
Fuertes's Water Filtration Works	12mo,	2 50
Gerhard's Sanitary House Inspection	12mo,	1 00
Godwin's Railroad Engineer's Field-book	16mo, morocco,	2 50
Goodrich's Economic Disposal of Towns' Refuse	Demy 8vo,	3 50
Gore's Elements of Geodesy	8vo,	2 50
Hazlehurst's Towers and Tanks for Cities and Towns	8vo,	2 50
Howard's Transition Curve Field-book	16mo, morocco,	1 50
Howe's Retaining Walls (New Edition.)	12mo,	1 25
Hudson's Excavation Tables. Vol. II.	8vo,	1 00
Hutton's Mechanical Engineering of Power Plants	8vo,	5 00
" Heat and Heat Engines	8vo,	5 00
Johnson's Materials of Construction	8vo,	6 00
" Theory and Practice of Surveying	Small 8vo,	4 00
Kent's Mechanical Engineer's Pocket-book	16mo, morocco,	5 00
Kiersted's Sewage Disposal	12mo,	1 25
Mahan's Civil Engineering. (Wood.)	8vo,	5 00
Merriman and Brook's Handbook for Surveyors.	16mo, mor.,	2 00
Merriman's Precise Surveying and Geodesy	8vo,	2 50
" Sanitary Engineering	8vo,	2 00
Nagle's Manual for Railroad Engineers	16mo, morocco,	3 00
Ogden's Sewer Design	12mo,	2 00
Patton's Civil Engineering	8vo, half morocco,	7 50
" Foundations	8vo,	5 00
Philbrick's Field Manual for Engineers	16mo, morocco,	3 00
Pratt and Alden's Street-railway Road-beds	8vo,	2 00
Rockwell's Roads and Pavements in France	12mo,	1 25
Schuyler's Reservoirs for Irrigation	Large 8vo,	5 00
Searles's Field Engineering	16mo, morocco,	3 00
" Railroad Spiral	16mo, morocco,	1 50
Siebert and Biggin's Modern Stone Cutting and Masonry ..	8vo,	1 50
Smart's Engineering Laboratory Practice	12mo,	2 50
Smith's Wire Manufacture and Uses	Small 4to,	3 00
Spalding's Roads and Pavements	12mo,	2 00

Spalding's Hydraulic Cement	12mo,	\$2 00
Taylor's Prismoïdal Formulas and Earthwork.....	8vo,	1 50
Thurston's Materials of Construction	8vo,	5 00
Tillson's Street Pavements and Paving Materials	8vo,	4 00
* Trautwine's Civil Engineer's Pocket-book....	16mo, morocco,	5 00
* " " Cross-section.....	Sheet,	25
* " " Excavations and Embankments.....	8vo,	2 00
* " " Laying Out Curves.....	12mo, morocco,	2 50
Turneure and Russell's Public Water-supplies.....	8vo,	5 00
Waddell's De Pontibus (A Pocket-book for Bridge Engineers).		
	16mo, morocco,	3 00
Wait's Engineering and Architectural Jurisprudence.....	8vo,	6 00
	Sheep,	6 50
" Law of Field Operati in Engineering, etc.....	8vo,	5 00
	Sheep,	5 50
Warren's Stereotomy—Stone-cutting.....	8vo,	2 50
Webb's Engineering Instruments. New Edition. 16mo, morocco,		1 25
" Railroad Construction.....	8vo,	4 00
Wegmann's Construction of Masonry Dams.....	4to,	5 00
Wellington's Location of Railways.....	Small 8vo,	5 00
Wheeler's Civil Engineering.....	8vo,	4 00
Wilson's Topographical Surveying.....	8vo,	3 50
Wolf's Windmill as a Prime Mover,.....	8vo,	3 00

HYDRAULICS.

(See also ENGINEERING, p. 7.)

Bazin's Experiments upon the Contraction of the Liquid Vein.		
(Trautwine.).....	8vo,	2 00
Bovey's Treatise on Hydraulics.....	8vo,	4 00
Church's Mechanics of Engineering, Solids, and Fluids....	8vo,	6 00
Coffin's Graphical Solution of Hydraulic Problems.....	12mo,	2 50
Ferrel's Treatise on the Winds, Cyclones, and Tornadoes....	8vo,	4 00
Folwell's Water Supply Engineering.....	8vo,	4 00
Frizell's Water-power.....	8vo,	5 00
Fuertes's Water and Public Health.....	12mo,	1 50
" Water Filtration Works.....	12mo,	2 50
Ganguillet & Kutter's Flow of Water. (Hering & Trautwine.)		
	8vo,	4 00
Hazen's Filtration of Public Water Supply.....	8vo,	3 00
Hazlehurst's Towers and Tanks for Cities and Towns.....	8vo,	2 50
Herschel's 115 Experiments	8vo,	2 00
Kiersted's Sewage Disposal.....	12mo,	1 25
Mason's Water Supply.....	8vo,	5 00
" Examination of Water.....	12mo,	1 25
Merriman's Treatise on Hydraulics.....	8vo,	4 00

Nichols's Water Supply (Chemical and Sanitary).....	8vo,	\$2 50
Schuyler's Reservoirs for Irrigation	Large 8vo,	5 00
Turneure and Russell's Public Water-supplies.....	8vo,	5 00
Wegmann's Water Supply of the City of New York	4to,	10 00
Weisbach's Hydraulics. (Du Bois.).....	8vo,	5 00
Whipple's Microscopy of Drinking Water	8vo,	3 50
Wilson's Irrigation Engineering.....	8vo,	4 00
" Hydraulic and Placer Mining.....	12mo,	2 00
Wolff's Windmill as a Prime Mover.....	8vo,	3 00
Wood's Theory of Turbines.....	8vo,	2 50

LAW.

Davis's Elements of Law.....	8vo,	2 50
" Treatise on Military Law.....	8vo,	7 00
	Sheep,	7 50
Manual for Courts-martial.....	16mo, morocco,	1 50
Wait's Engineering and Architectural Jurisprudence.....	8vo,	6 00
	Sheep,	6 50
" Law of Contracts	8vo,	3 00
" Law of Operations Preliminary to Construction in En- gineering and Architecture.....	8vo,	5 00
	Sheep,	5 50
Winthrop's Abridgment of Military Law.....	12mo,	2 50

MANUFACTURES.

Allen's Tables for Iron Analysis.....	8vo,	3 00
Beaumont's Woollen and Worsted Manufacture.....	12mo,	1 50
Bolland's Encyclopædia of Founding Terms.....	12mo,	3 00
" The Iron Founder.....	12mo,	2 50
" " " " " Supplement.....	12mo,	2 50
Eissler's Explosives, Nitroglycerine and Dynamite.....	8vo,	4 00
Ford's Boiler Making for Boiler Makers.....	18mo,	1 00
Metcalf's Cost of Manufactures.....	8vo,	5 00
Metcalf's Steel—A Manual for Steel Users.....	12mo,	2 00
* Reisig's Guide to Piece Dyeing.....	8vo,	25 00
Spencer's Sugar Manufacturer's Handbook	16mo, morocco,	2 00
" Handbook for Chemists of Beet Sugar Houses. 16mo, morocco,		3 00
Thurston's Manual of Steam Boilers.....	8vo,	5 00
Walke's Lectures on Explosives.....	8vo,	4 00
West's American Foundry Practice.....	12mo,	2 50
" Moulder's Text-book	12mo,	2 50
Wiechmann's Sugar Analysis.....	Small 8vo,	2 50
Woodbury's Fire Protection of Mills.....	8vo,	2 50

MATERIALS OF ENGINEERING.

(See also ENGINEERING, p. 7.)

Baker's Masonry Construction.....	8vo,	\$5 00
Bovey's Strength of Materials.....	8vo,	7 50
Burr's Elasticity and Resistance of Materials.....	8vo,	5 00
Byrne's Highway Construction.....	8vo,	5 00
Church's Mechanics of Engineering—Solids and Fluids.....	8vo,	6 00
Du Bois's Stresses in Framed Structures.....	Small 4to,	10 00
Johnson's Materials of Construction.....	8vo,	6 00
Lanza's Applied Mechanics.....	8vo,	7 50
Martens's Testing Materials. (Henning.).....	2 vols., 8vo,	7 50
Merrill's Stones for Building and Decoration.....	8vo,	5 00
Merriman's Mechanics of Materials.....	8vo,	4 00
“ Strength of Materials.....	12mo,	1 00
Patton's Treatise on Foundations.....	8vo,	5 00
Rockwell's Roads and Pavements in France.....	12mo,	1 25
Spalding's Roads and Pavements.....	12mo,	2 00
Thurston's Materials of Construction.....	8vo,	5 00
“ Materials of Engineering.....	3 vols., 8vo,	8 00
Vol. I., Non-metallic.....	8vo,	2 00
Vol. II., Iron and Steel.....	8vo,	3 50
Vol. III., Alloys, Brasses, and Bronzes.....	8vo,	2 50
Wood's Resistance of Materials.....	8vo,	2 00

MATHEMATICS.

Baker's Elliptic Functions.....	8vo,	1 50
*Bass's Differential Calculus.....	12mo,	4 00
Briggs's Plane Analytical Geometry.....	12mo,	1 00
Chapman's Theory of Equations.....	12mo,	1 50
Compton's Logarithmic Computations.....	12mo,	1 50
Davis's Introduction to the Logic of Algebra.....	8vo,	1 50
Halsted's Elements of Geometry.....	8vo,	1 75
" Synthetic Geometry.....	8vo,	1 50
Johnson's Curve Tracing.....	12mo,	1 00
" Differential Equations—Ordinary and Partial.		
	Small 8vo,	3 50
" Integral Calculus.....	12mo,	1 50
" " Unabridged. Small 8vo. (<i>In press.</i>)		
" Least Squares.....	12mo,	1 50
*Ludlow's Logarithmic and Other Tables. (Bass.).....	8vo,	2 00
* " Trigonometry with Tables. (Bass.).....	8vo,	3 00
*Mahan's Descriptive Geometry (Stone Cutting).....	8vo,	1 50
Merriman and Woodward's Higher Mathematics.....	8vo,	5 00

Merriman's Method of Least Squares8vo,	\$2 00
Rice and Johnson's Differential and Integral Calculus,		
" 2 vols. In 1, small 8vo,	2 50	
" Differential Calculus.....	Small 8vo,	3 00
" Abridgment of Differential Calculus.		
	Small 8vo,	1 50
Totten's Metrology.....	.8vo,	2 50
Warren's Descriptive Geometry.....	2 vols., 8vo,	3 50
" Drafting Instruments.....	12mo,	1 25
" Free-hand Drawing.....	12mo,	1 00
" Linear Perspective.....	12mo,	1 00
" Primary Geometry.....	12mo,	75
" Plane Problems	12mo,	1 25
" Problems and Theorems.....	.8vo,	2 50
" Projection Drawing.....	12mo,	1 50
Wood's Co-ordinate Geometry.....	.8vo,	2 00
" Trigonometry.....	12mo,	1 00
Woolf's Descriptive Geometry.....	Large 8vo,	3 00

MECHANICS—MACHINERY.

(See also ENGINEERING, p. 7.)

Baldwin's Steam Heating for Buildings.....	12mo,	2 50
Barr's Kinematics of Machinery.....	.8vo,	2 50
Benjamin's Wrinkles and Recipes	12mo,	2 00
Chordal's Letters to Mechanics.....	12mo,	2 00
Church's Mechanics of Engineering.....	.8vo,	6 00
" Notes and Examples in Mechanics.....	.8vo,	2 00
Crehore's Mechanics of the Girder.....	.8vo,	5 00
Cromwell's Belts and Pulleys.....	12mo,	1 50
" Toothed Gearing.....	12mo,	1 50
Compton's First Lessons in Metal Working.....	12mo,	1 50
Compton and De Groodt's Speed Lathe.....	12mo,	1 50
Dana's Elementary Mechanics	12mo,	1 50
Dingey's Machinery Pattern Making.....	12mo,	2 00
* Dredge's Trans. Exhibits Building, World Exposition.		
	Large 4to, half morocco,	5 00
Du Bois's Mechanics. Vol. I., Kinematics8vo,	3 50
" " Vol. II., Statics.....	.8vo,	4 00
" " Vol. III., Kinetics.....	.8vo,	3 50
Fitzgerald's Boston Machinist.....	18mo,	1 00
Flather's Dynamometers.....	12mo,	2 00
" Rope Driving.....	12mo,	2 00
Hall's Car Lubrication.....	12mo,	1 00
Holby's Saw Filing	18mo,	75

* Johnson's Theoretical Mechanics. An Elementary Treatise.	12mo,	\$3 00
Jones's Machine Design. Part I., Kinematics.....	8vo,	1 50
“ “ “ Part II., Strength and Proportion of Machine Parts.....	8vo,	3 00
Lanza's Applied Mechanics	8vo,	7 50
MacCord's Kinematics.....	8vo,	5 00
Merriman's Mechanics of Materials.....	8vo,	4 00
Metcalf's Cost of Manufactures.....	8vo,	5 00
* Michie's Analytical Mechanics.....	8vo,	4 00
Richards's Compressed Air.....	12mo,	1 50
Robinson's Principles of Mechanism.....	8vo,	3 00
Smith's Press-working of Metals.....	8vo,	3 00
Thurston's Friction and Lost Work.....	8vo,	3 00
“ The Animal as a Machine	12mo,	1 00
Warren's Machine Construction.....	2 vols., 8vo,	7 50
Weisbach's Hydraulics and Hydraulic Motors. (Du Bois.)..	8vo,	5 00
“ Mechanics of Engineering. Vol. III., Part I., Sec. I. (Klein.)....	8vo,	5 00
Weisbach's Mechanics of Engineering. Vol. III., Part I., Sec. II. (Klein.)....	8vo,	5 00
Weisbach's Steam Engines. (Du Bois.).....	8vo,	5 00
Wood's Analytical Mechanics.....	8vo,	3 00
“ Elementary Mechanics.....	12mo,	1 25
“ “ “ Supplement and Key....	12mo,	1 25

METALLURGY.

Allen's Tables for Iron Analysis.....	8vo,	3 00
Egleston's Gold and Mercury.....	Large 8vo,	7 50
“ Metallurgy of Silver.....	Large 8vo,	7 50
* Kerl's Metallurgy—Steel, Fuel, etc.....	8vo,	15 00
Kunhardt's Ore Dressing in Europe.....	8vo,	1 50
Metcalf's Steel—A Manual for Steel Users.....	12mo,	2 00
O'Driscoll's Treatment of Gold Ores.....	8vo,	2 00
Thurston's Iron and Steel.....	8vo,	3 50
“ Alloys.....	8vo,	2 50
Wilson's Cyanide Processes.....	12mo,	1 50

MINERALOGY AND MINING.

Barringer's Minerals of Commercial Value....Oblong morocco,	2 50
Beard's Ventilation of Mines.....12mo,	2 50
Boyd's Resources of South Western Virginia.....8vo,	3 00
“ Map of South Western Virginia....Pocket-book form,	2 00
Brush and Penfield's Determinative Mineralogy. New Ed. 8vo,	4 00

Chester's Catalogue of Minerals.....	8vo,	\$1 25
“ “ “ “	Paper,	50
“ Dictionary of the Names of Minerals.....	8vo,	3 00
Dana's American Localities of Minerals.....	Large 8vo,	1 00
“ Descriptive Mineralogy. (E. S.) Large 8vo. half morocco,		12 50
“ First Appendix to System of Mineralogy.....	Large 8vo,	1 00
“ Mineralogy and Petrography. (J. D.).....	12mo,	2 00
“ Minerals and How to Study Them. (E. S.).....	12mo,	1 50
“ Text-book of Mineralogy. (E. S.)... New Edition.	8vo,	4 00
* Drinker's Tunnelling, Explosives, Compounds, and Rock Drills.		
4to, half morocco,		25 00
Egleston's Catalogue of Minerals and Synonyms.....	8vo,	2 50
Eissler's Explosives--Nitroglycerine and Dynamite.....	8vo,	4 00
Hussak's Rock-forming Minerals. (Smith.).....	Small 8vo,	2 00
Ihlseng's Manual of Mining.. ..	8vo,	4 00
Kunhardt's Ore Dressing in Europe.....	8vo,	1 50
O'Driscoll's Treatment of Gold Ores.....	8vo,	2 00
* Penfield's Record of Mineral Tests.....	Paper, 8vo,	50
Rosenbusch's Microscopical Physiography of Minerals and Rocks. (Iddings.).....	8vo,	5 00
Sawyer's Accidents in Mines.....	Large 8vo,	7 00
Stockbridge's Rocks and Soils.....	8vo,	2 50
*Tillman's Important Minerals and Rocks.....	8vo,	2 00
Walke's Lectures on Explosives.....	8vo,	4 00
Williams's Lithology.....	8vo,	3 00
Wilson's Mine Ventilation.....	12mo,	1 25
“ Hydraulic and Placer Mining.....	12mo,	2 50

STEAM AND ELECTRICAL ENGINES, BOILERS, Etc.

(See also ENGINEERING, p. 7.)

Baldwin's Steam Heating for Buildings.....	12mo,	2 50
Clerk's Gas Engine.....	Small 8vo,	4 00
Ford's Boiler Making for Boiler Makers.....	18mo,	1 00
Hemenway's Indicator Practice.....	12mo,	2 00
Kent's Steam-boiler Economy.....	8vo,	4 00
Kneass's Practice and Theory of the Injector.....	8vo,	1 50
MacCord's Slide Valve.....	8vo,	2 00
Meyer's Modern Locomotive Construction.....	4to,	10 00
Peabody and Miller's Steam-boilers.....	8vo,	4 00
Peabody's Tables of Saturated Steam.....	8vo,	1 00
“ Thermodynamics of the Steam Engine.....	8vo,	5 00
“ Valve Gears for the Steam Engine.....	8vo,	2 50
“ Manual of the Steam-engine Indicator.....	12mo,	1 50
Pray's Twenty Years with the Indicator.....	Large 8vo,	2 50

Pupin and Osterberg's Thermodynamics.....	12mo,	\$1 25
Reagan's Steam and Electric Locomotives.....	12mo,	2 00
Röntgen's Thermodynamics. (Du Bois.).....	8vo,	5 00
Sinclair's Locomotive Running.....	12mo,	2 00
Snow's Steam-boiler Practice.....	8vo,	3 00
Thurston's Boiler Explosions.....	12mo,	1 50
“ Engine and Boiler Trials.....	8vo,	5 00
“ Manual of the Steam Engine. Part I., Structure and Theory.....	8vo,	6 00
“ Manual of the Steam Engine. Part II., Design, Construction, and Operation.....	8vo,	6 00
	2 parts,	10 00
“ Philosophy of the Steam Engine.....	12mo,	75
“ Reflection on the Motive Power of Heat. (Carnot.) 12mo,		1 50
“ Stationary Steam Engines.....	8vo,	2 50
“ Steam-boiler Construction and Operation.....	8vo,	5 00
Spangler's Valve Gears.....	8vo,	2 50
“ Notes on Thermodynamics.....	12mo,	1 00
Weisbach's Steam Engine. (Du Bois.).....	8vo,	5 00
Whitham's Steam-engine Design.....	8vo,	5 00
Wilson's Steam Boilers. (Flather.).....	12mo,	2 50
Wood's Thermodynamics, Heat Motors, etc.....	8vo,	4 00

TABLES, WEIGHTS, AND MEASURES.

Adriance's Laboratory Calculations.....	12mo,	1 25
Allen's Tables for Iron Analysis.....	8vo,	3 00
Bixby's Graphical Computing Tables.....	Sheet,	25
Compton's Logarithms.....	12mo,	1 50
Crandall's Railway and Earthwork Tables.....	8vo,	1 50
Davis's Elevation and Stadia Tables.....	Small 8vo,	1 00
Fisher's Table of Cubic Yards.....	Cardboard,	25
Hudson's Excavation Tables. Vol. II.....	8vo,	1 00
Johnson's Stadia and Earthwork Tables.....	8vo,	1 25
Ludlow's Logarithmic and Other Tables. (Bass.).....	12mo,	2 00
Totten's Metrology.....	8vo,	2 50

VENTILATION.

Baldwin's Steam Heating.....	12mo,	2 50
Beard's Ventilation of Mines.....	12mo,	2 50
Carpenter's Heating and Ventilating of Buildings.....	8vo,	3 00
Gerhard's Sanitary House Inspection.....	12mo,	1 00
Wilson's Mine Ventilation.....	12mo,	1 25

MISCELLANEOUS PUBLICATIONS.

Alcott's Gems, Sentiment, Language.....	Gilt edges,	\$5 00
Emmon's Geological Guide-book of the Rocky Mountains..	8vo,	1 50
Ferrel's Treatise on the Winds.....	8vo,	4 00
Haines's Addresses Delivered before the Am. Ry. Assn....	12mo,	2 50
Mott's The Fallacy of the Present Theory of Sound..	Sq. 16mo,	1 00
Richards's Cost of Living.....	12mo,	1 00
Ricketts's History of Rensselaer Polytechnic Institute....	8vo,	3 00
Rotherham's The New Testament Critically Emphasized.		
	12mo,	1 50
" The Emphasized New Test. A new translation.		
	Large 8vo,	2 00
Totten's An Important Question in Metrology.....	8vo,	2 50

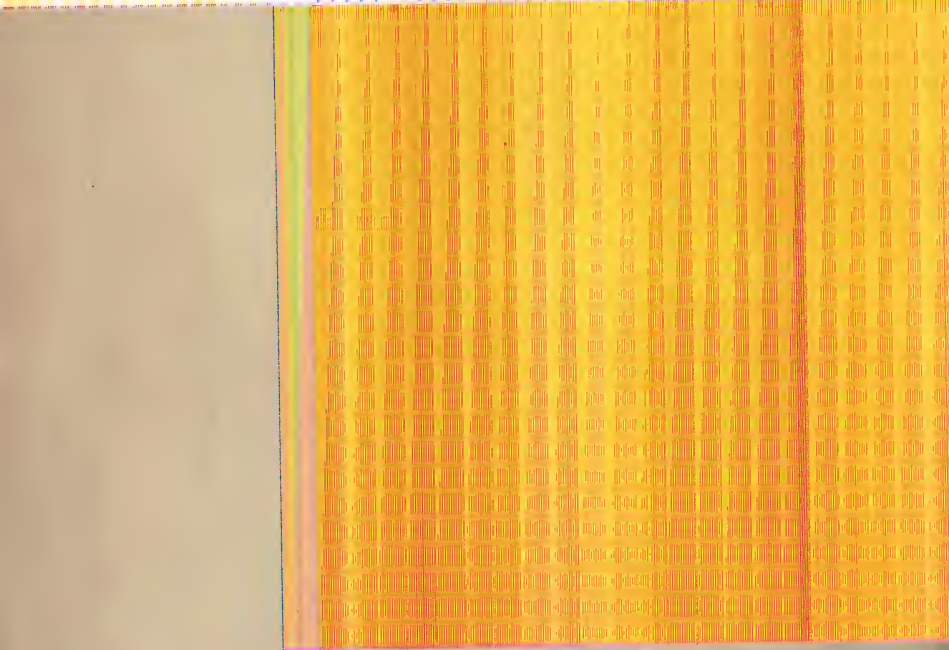
HEBREW AND CHALDEE TEXT-BOOKS.

FOR SCHOOLS AND THEOLOGICAL SEMINARIES.

Gesenius's Hebrew and Chaldee Lexicon to Old Testament. (Tregelles.).....	Small 4to, half morocco,	5 00
Green's Elementary Hebrew Grammar.....	12mo,	1 25
" Grammar of the Hebrew Language (New Edition).	8vo,	3 00
" Hebrew Chrestomathy.....	8vo,	2 00
Letteris's Hebrew Bible (Massoretic Notes in English).		
	8vo, arabesque,	2 25

MEDICAL.

Hammarsten's Physiological Chemistry. (Mandel.).....	8vo,	4 00
Mott's Composition, Digestibility, and Nutritive Value of Food.		
	Large mounted chart,	1 25
Ruddiman's Incompatibilities in Prescriptions.....	8vo,	2 00
Steel's Treatise on the Diseases of the Dog.....	8vo,	3 50
Woodhull's Military Hygiene.....	16mo,	1 50
Worcester's Small Hospitals—Establishment and Maintenance, including Atkinson's Suggestions for Hospital Archi- tecture.....	12mo,	1 25





90706 C W4554kx
Author Wells, Horace Lemuel
Title A laboratory guide in qualitative chemical analysis

M.S.C. 23.11.38.
University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
Under Pa*, "Ref. Index File"
Made by LIBRARY BUREAU

